Appendix 2 show that the use of HiTEC 3000 in unleaded gasoline will not cause or contribute to the failure of emission control systems or devices to meet applicable emission standards.

BACKGROUND AND PURPOSE

The EPA's previous analysis of fuel or fuel additive waiver requests has limited consideration of the air quality benefits that may occur from the "general use" of the approved product. Instead, they have relied heavily on the use of "reliable statistical sampling and fleet testing protocols" to achieve the proof required by an applicant to demonstrate that his product will not cause or contribute to failure of emission control systems and thereby adversely affect air quality (45 Federal Registrar, 1980).

Systems Applications, Inc. (SAI) was retained by Ethyl Petroleum Additives, Inc. to estimate the effects of HiTEC 3000 use on ambient air quality through the use of SAI's Urban Airshed Model (UAM-CB-IV). Since 1984, the EPA's Office of Air Quality Planning and Standards (OAQPS) has adopted the UAM as the preferred model for "photochemical pollutant modeling applications involving entire urban areas" (EPA, 1986), and has commented that the UAM "is the most widely applied and evaluated photochemical dispersion model in existence." (Seinfeld, 1988; Burton, 1988).

The estimation of the effects of HiTEC 3000 use in unleaded gasoline is of particular importance to this waiver application because it directly addresses the potential air quality improvements from the use of HiTEC 3000 on urban and/or regional reductions in ambient ozone, carbon monoxide (CO), NO_x and Mn. In addition, these analyses focus on the fundamental purpose of the Federal Motor Vehicle Control Program which is to improve and maintain air quality.

DESCRIPTION OF THE URBAN AIRSHED MODEL

The Urban Airshed Model (UAM) is a three-dimensional grid (Eulerian) model designed to calculate the concentrations of both inert and chemically reactive

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pollutants by simulating the physical and chemical processes in the atmosphere that affect pollutant concentrations. The basis for the UAM is the atmospheric diffusion (species continuity or advection/diffusion) equation. This equation represents a mass balance in which all of the relevant emissions, transport, diffusion, chemical reactions, and removal processes are expressed in mathematical terms as follows:

$$\underset{\substack{\text{Time} \\ \text{Dependence}}}{\underbrace{\frac{\partial c_i}{\partial t}}} + \underset{\text{Advection}}{\underbrace{\frac{\partial(uc_i)}{\partial x} + \frac{\partial(vc_i)}{\partial y} + \frac{\partial(wc_i)}{\partial z}}}$$

$$= \underset{\text{Turbulent Diffusion}}{\underbrace{\frac{\partial}{\partial x}\left(K_H \frac{\partial c_i}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_H \frac{\partial c_i}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_V \frac{\partial c_i}{\partial z}\right)}}$$

$$+ \underset{\substack{\text{Chemical} \\ \text{Reaction}}}{\underbrace{R_i}} + \underset{\text{Emissions}}{\underbrace{S_i}} + \underset{\substack{\text{Pollutant} \\ \text{Sinks}}}{\underbrace{L_i}}$$

where c_i represents the pollutant concentration and is a function of space (x,y,z) and time (t). The other terms in this equation are

u,v,w = horizontal and vertical wind speed components

K_H, K_V = horizontal and vertical turbulent diffusion

R_i = net rate of production of pollutant i by chemical reactions

S_i = emissions rate of pollutant i

L_i = net rate of removal of pollutant i by surface uptake processes

Much of the current interest in the UAM arises from the need to calculate the effects of emission scenarios on urban ozone concentrations as part of environmental assessment studies such as State Implementation Plans (SIPs) or the evaluation of different emission control strategies. The UAM has also been sucessfully used to determine emission control strategies for inert and semi-inert compounds, e.g., CO (Ireson et al., 1987). Elevated ozone concentrations are usually due to the interaction of Volatile Organic Compounds (VOCs) (including pure and oxygenated

hydrocarbons and other hydrocarbon derivatives) and Nitrogen Oxides (NO_x). The main factors that affect photochemical air quality include:

- The spatial and temporal distribution of emissions of NO_x and VOC (both anthropogenic and biogenic),
- The composition of the emitted VOC and NO_x,
- The spatial and temporal variations in the wind fields,
- The dynamics of the boundary layer including stability and the level of mixing,
- The chemical reactions involving VOC, NO_x, and other important species,
- The diurnal variations of solar insolation and temperature,
- The loss of ozone and ozone precursors by dry deposition, and
- The ambient background of VOC, NO_x, and other species in, immediately upwind, and above the region of study.

Because the UAM provides state-of-the-science mathematical representation of the above processes, its use is appropriate for the analysis of alternative emission scenarios, such as the use of HiTEC 3000, on urban air quality. The UAM can account for the effects on ozone and NO_2 air quality of temporally varying mass emission rates as well as differences in the composition and locations (e.g., surface based versus elevated) of the emissions. Figure 1-1 contains a schematic illustration of the basic features of the UAM to simulate air quality in an urban area. The development of the UAM during the 1970's was supported by the U.S. EPA. More recently, the UAM was updated to include a more complete treatment of chemistry, the Carbon Bond IV chemical mechanism (Gery, Whitten, and Killus, 1988), and advection/diffusion (Smolarkiewicz, 1983). A complete description of the UAM is contained in a series of research reports that are referenced in the UAM User's Guides (Ames et al., 1985).

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A. The Area to Be Modeled

B. Specification of the Grid
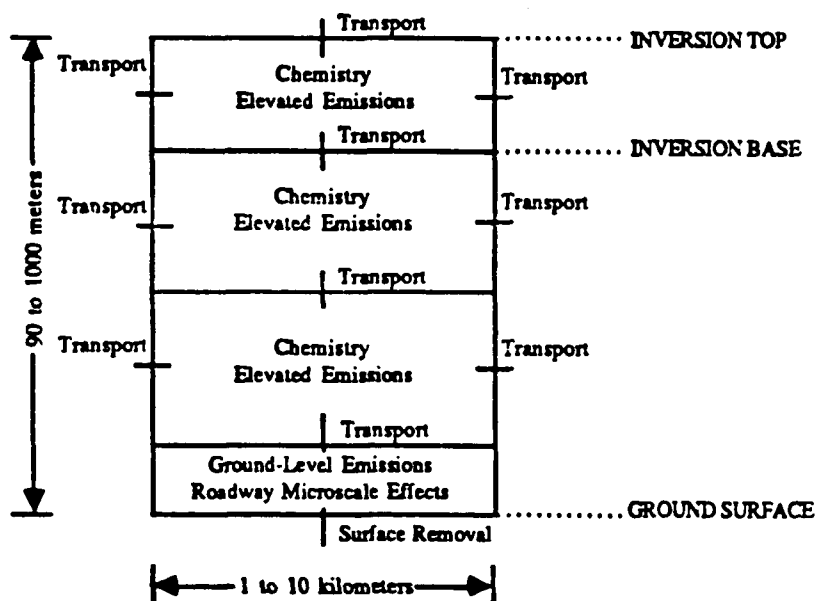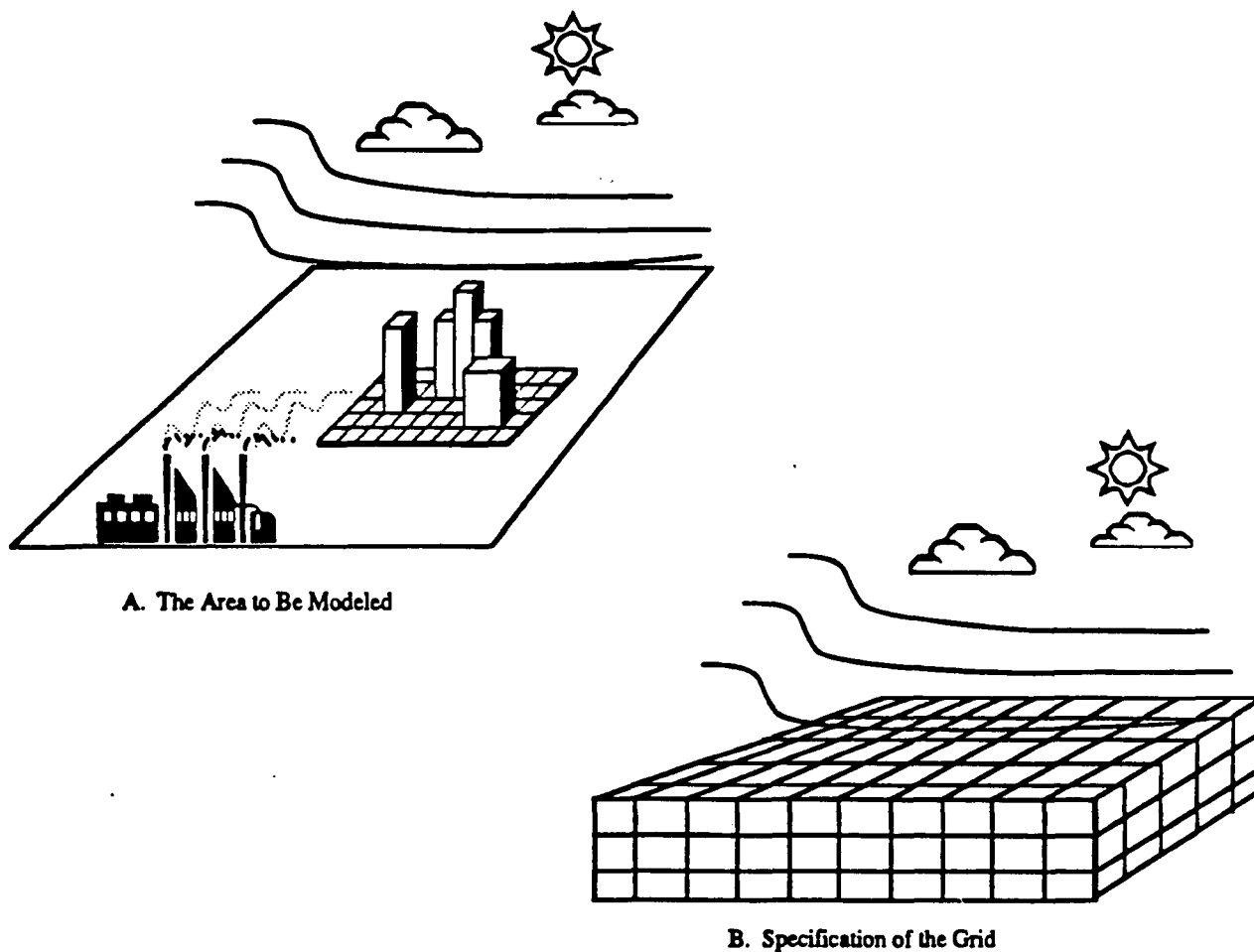
C. Atmospheric Processes Treated in a Column of Grid Cells

FIGURE 1-1. Schematic illustration of the use of the grid and treatment of atmospheric processes in the Urban Airshed Model.

2 SELECTION OF CITIES TO EVALUATE THE EFFECTS OF HiTEC 3000 ON URBAN AIR QUALITY

One of the first tasks in evaluating the effects of HiTEC 3000 on urban air quality is the selection of cities to apply the Urban Airshed Model (UAM) for a future year emission scenario reflecting the effects of current gasoline and the use of HiTEC 3000. For this study we wish to select cities that represent typical conditions for cities with urban air quality problems that may potentially use HiTEC 3000. Originally, multiple cities were considered for use. Calculations for the first city, selected because of the timely availability of the needed air quality and meteorological data bases, were performed and presented to the EPA in the fall of 1989. The results for the first city indicated that HiTEC 3000 had essentially no measurable effect on urban air quality (based on the sensitivity of routinely operatory ozone monitors.) Thus because of the small effect, with the concurrence of the EPA, just two cities were used to simulate the effect of HiTEC 3000 on urban air quality.

CITY SELECTION CRITERIA

The UAM modeling data bases used to evaluate the effects of HiTEC 3000 on urban air quality were selected out of practical necessity from existing data sets. We have identified the following nine criteria for selecting the UAM data bases (cities):

1. **Data availability:** Currently available high quality UAM(CB-IV) emissions, air quality, and meteorological modeling inputs are required.

2. **High current design value:** Cities with higher ozone concentrations are preferable over cities that are near attainment.

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3. **Emissions growth and percent automotive emissions:** Cities whose emissions are dominated by the mobile sources are preferable over cities dominated by other sources.

4. **Atmospheric reactivity:** Cities with different atmospheric reactivities are of interest.

5. **Influence of transport:** Episodes that are dominated by transport (boundary conditions) are not as desirable due to technical difficulties in defining emission scenarios.

6. **Influence of biogenics:** Cities that are highly influenced by biogenic emissions are not as desirable due to large uncertainties in the biogenic emission rates and composition.

7. **Model performance:** Episodes with "good" model performance are preferable over those with "questionable" model performance.

8. **Potential use of HiTEC 3000:** Cities that may potentially use HiTEC 3000 are preferred.

9. **"Bush" Bill:** The current administration has identified nine regions (Greater Connecticut, New York, Philadelphia, Baltimore, Milwaukee, Chicago, Houston, San Diego, and Los Angeles) that have severe ozone problems and have been targeted for possible use of alternative fuels. It is desirable to use one or more of these cities to evaluate the effects of HiTEC 3000.

CANDIDATE CITIES

Of these criteria the most important is the first: the availability of high quality UAM inputs. In particular, high quality emission inputs, including raw data, which can be modified to reflect the effects of the Ethyl Corporation fleet testing program

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vehicle test data are needed. Starting with over 60 UAM data basis available at Systems Applications, Inc., nine candidate UAM modeling data bases were identified which contain sufficient detail in the emission inputs to satisfy the needs of evaluating the effects of HiTEC 3000 on air quality. Pertinent information concerning these nine candidate cities and their relationship to the city selection criteria are contained in Table 2-1 and Figures 2-1.

After examining the relationship between the candidate cities and the city selection criteria it immediately becomes apparent that Los Angeles satisfies almost all of the selection criteria: the highest observed ozone concentrations (design value); large influence from mobile sources; and is minimally influenced by transport and biogenics. However, HiTEC 3000 can not be used in California, thus the use of California cities (Los Angeles, San Diego, Santa Barabara-Ventura, and the San Francisco Bay Area) receives low priority. This results in five candidate cities for consideration of the highest priority: St. Louis, Philadelphia, New York, Dallas-Fort Worth, and Atlanta.

NORTHEAST CORRIDOR AREA

One of the regions with the most severe ozone attainment problem are cities in the northeast corridor area of the eastern U.S. (Los Angeles, Houston, and Chicago also have severe ozone attainment problems). Due to the large number of nonattainment regions and the high population density in the northeast U.S., it is desirable to pick a city that has reactivity conditions representative of cities in the northeast corridor. In particular, because it has the fourth highest design value in the U.S., the New York region is highly desirable.

Several UAM modeling data bases using 1980 data were developed as part of the Oxidant Modeling of the New York Metropolitan Area Program (OMNYMAP) (Rao, 1987) with one data set improved slightly under the EPA Five Cities UAM Study (Morris et al., 1989). However, there is considerable questions concerning the validity of the these UAM inputs (ESEERCO, 1989). The OMNYMAP UAM inputs used a very simplistic representation of meteorolgoical conditions (horizontally and vertically

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TABLE 2-1. Comparison of selection criteria for the candidate cities.

City	Base Case Episode	1985 Median Measured VOC-to-NOx Ratio[a]	Pertinent Anthropogenic Emission Scenarios						Influence of Transport	Significance of Biogenics (%)[b]	Bush Bill	1988 Design Value (ppm)
			Scenario	VOC (TPD)	NOx (TPD)	VOC/NOx Ratio	% Mobile VOC	% Mobile NOx				
Los Angeles	June 5-7 1985	10.3[d]	1985 Base	1423	1063	3.8	52	61	Low	Low (0)	YES	0.34
			2000 Base	1019	904	3.2	36	72				
			2000 Tier 1	408	357	3.3	38	54				
			2010 Base	1154	1033	3.2	39	74				
			2010 Tier 1	627	470	3.8	30	53				
			2010 Tier 2	401	312	3.7	36	46				
			2010 Tier 3	200	195	2.9	38	28				
Dallas-Fort Worth	August 29-31 1985	11.8	1985 Base	1434	890	4.6	64	43	Low	Low (33)	NO	0.14
			1995 Base	991	852	3.3	38	29		(41)		
Santa Barbara Ventura	September 22-24 1985	9.5[d]	1985 Base	228	87	6.7	46	21	Medium	High (NA)	NO	0.13
San Francisco Bay Area	July 12-13 1984	--	1984 Base	NA	NA	NA	NA	NA	Medium	Medium (50)	NO	0.14
Atlanta	June 3-4 1984	10.4	1985 Base	1030	751	3.9	66	43	Low	High (55)	NO	0.166
			1995 Base	670	819	2.4	36	28		(66)		
San Diego	July 7-8 1983	--	1983 Base	233	1200	3.3	46	78	Medium	Medium (0)	YES	0.18
New York Metro. Area	August 8 1980	9.6[d]	1980 Base	2646	2342	3.2	47	40	High	Low (0)	YES,2	0.217
			1995 Base	3343	1183	8.1[e]	35	45				
Philadelphia AQCR	July 13 1979	8.0	1979 Base	1163	1077	3.1	NA	NA	High	Low (0)	YES	0.18
			1995 Base	2083	1385	4.3	24	41		Low (23)		
St. Louis	July 13 1976	9.6	1976 Base	656	1468[c]	1.3	57	23	Low	Low (0)	NO	0.159
			1995 Base	549	423	3.7	21	30		(14)		

a   The VOC/NOx ratios should be viewed with caution due to large spatial and temporal variations.
b   Percent biogenic VOC emissions is to total (biogenic plus anthropogenic) VOC emission inventory. (0) implies that the inventory did not includ biogenic emissions.
c   1979 St. Louis base case NOx emissions include significant amounts of elevated NOx emissions that lie outside of the modeling domain.
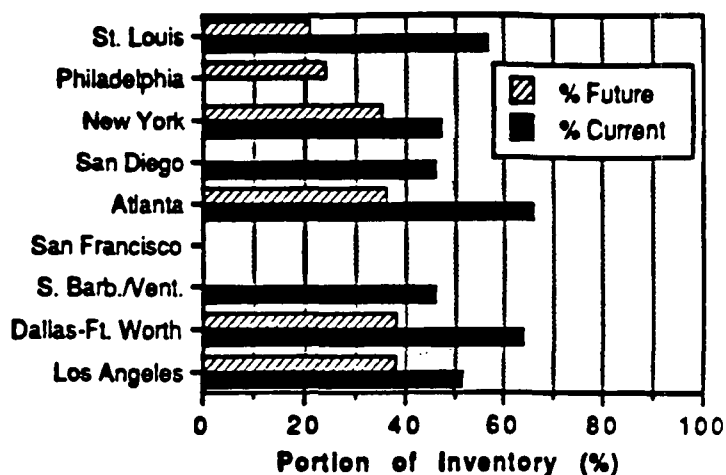d   1982 SIP value.
e   New York 1995 Base emission scenario contains an overestimate of the amount of running loss emissions.
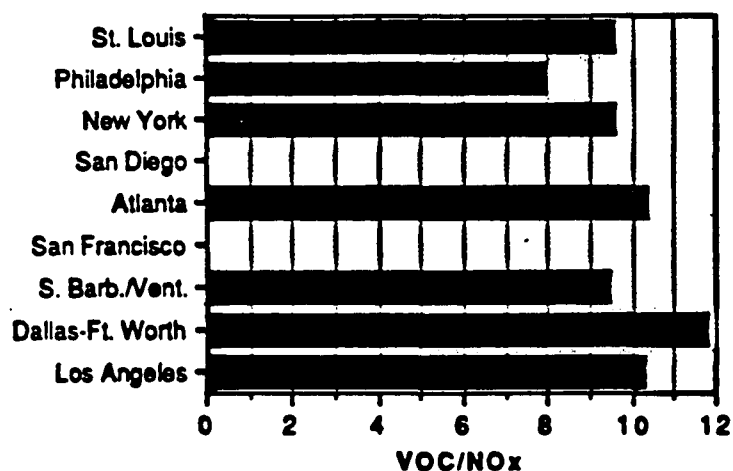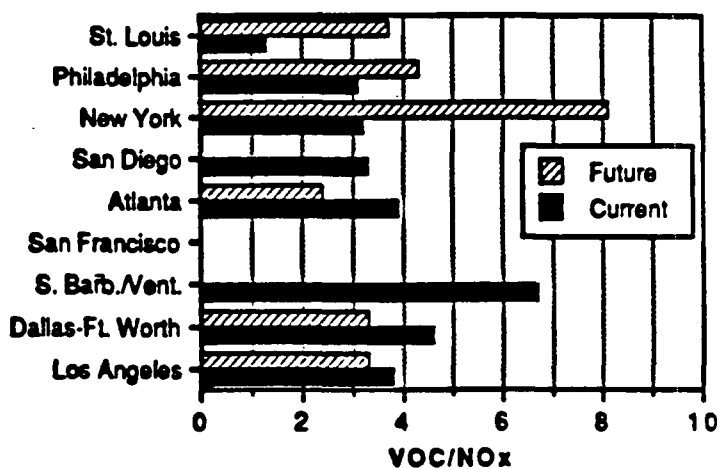
DESIGN VALUE AND BUSH BILL
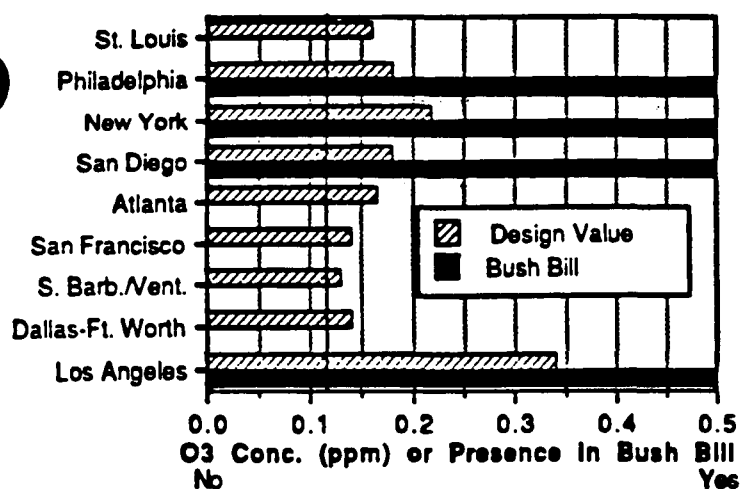
% MOBILE IN INVENTORY (VOC)

REACTIVITY (Current Air Quality)

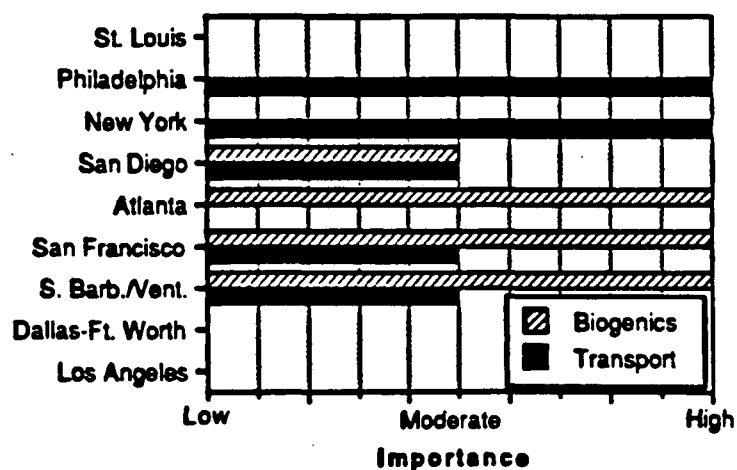## REACTIVITY (Emissions)

TRANSPORT AND BIOGENICS

FIGURE 2-1. Comparison of selection criteria for the candidate cities.

constant winds). More importantly, these New York UAM modeling data bases contain extremely high amounts of transported pollutants (i.e. boundary conditions) from outside the region. One of these New York UAM data bases was used to assess the effects of different Reid Vapor Pressure (RVP) values for gasoline fuel and alternative fuels (ethanol and ETBE) on urban air quality. Because of the high influence from boundary conditions (i.e. transport of pollutants from upwind areas), these alternative fuel scenarios showed almost no effect on urban air quality (Morris et al., 1989). Thus because UAM predicted ozone concentrations using the New York UAM data bases showed no effect to changes in mobile source emissions (e.g. the effect of HiTEC 3000) they are not appropriate for evaluating the effect of HiTEC 3000 on air quality.

Since it is important to include a city from the northeastern U.S. then one of the two Philadelphia UAM data bases should be considered. The two Philadelphia data bases can be characterized as a transport day (July 19, 1979) and a stagnation day (July 13 1979). Because the effects of changes in mobile source emissions will have very limited influence on the transport day, the stagnation episode should be considered. This data set has also been used in several EPA studies to evaluate the effects of alternative fuels, such as methanol (Whitten et al., 1986; Morris et al, 1990d) and compressed natural gas (Morris et al., 1990d), on urban air quality. The alternative fuels did have an affect on the predicted ozone concentrations indicating that mobile sources do have influence over urban air quality. Thus the Philadlephia stagnation episode was chosen as the first city to analyze the effects of HiTEC 3000 on air quality.

CANDIDATE CITIES

As shown in Table 2-1 and Figure 2-1, Philadelphia is a city that has a low measured VOC-to-NO_x ratio (i.e. reductions in NO_x emissions may increase ozone concentrations). Thus it was desirable to pick additional cities that have high VOC-to-NO_x ratios (i.e. reductions in NO_x emissions may decrease ozone concentrations) Of the cities listed in Table 2-1, Dallas-Fort Worth and Atlanta have the highest VOC-to-NO_x ratios. However, studies using the UAM for future year (1995) emission scenarios indicated that Dallas-Fort Worth behaved like a low VOC-to-NO_x ratio city

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(Morris et al., 1990a). Thus Atlanta was chosen as the second candidate city with Dallas-Fort Worth third. If additional analysis is waranted, optional cities of St. Louis and Los Angeles are available. Despite the fact that HiTEC 3000 can not be used in Los Angeles it is included as an optional city because of the many air quality studies performed there. This gives the following initial ordering of the candidate cities:

1. Philadelphia (stagnation episode)
2. Atlanta
3. Dallas-Fort Worth
4. St. Louis (optional)
5. Los Angeles (optional)

PRELIMINARY RESULTS

The Ethyl fleet testing program data out to 50,000 miles was used to define a 1994 emission scenario for Philadelphia. The Philadelphia scenario was run for a 1994 base case emission scenario (i.e. 9 RVP gasoline at normal octane) and a 1994 HiTEC 3000 emission scenario (i.e. 9 RVP gasoline with one point octane enhancement). Results from the Philadelphia simulation were presented to the EPA Office Of Mobile Sources (EPA/OMS) at a meeting in Washington DC on October 12 1989. At a subsequent meeting in Washington DC the Philadelphia and Atlanta results were presented to EPA/OMS and EPA Office of Air Quality and Planning Standards (EPA/OAQPS). Because the effect of HiTEC 3000 on emissions and urban air quality was small for these two cities, the EPA concluded that the use of more cities to analyze the effects of HiTEC 3000 was not warranted. Thus on the recommendation of the EPA, only two cities, Philadelphia and Atlanta, were used to assess the effects of HiTEC 3000 on urban air quality.

DEVELOPMENT OF UAM MODELING DATA BASES

The UAM modeling data bases for Philadelphia and Atlanta used in the analysis of the effect of HiTEC 3000 were originally developed by Systems Applications, Inc. for

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the EPA. The Philadelphia 13 July 1979 data base was developed using measured air quality and meteorological data from the Philadelphia Oxidant Study (Allard et al., 1981; Haney and Braverman 1985). The Atlanta UAM data base was developed as part of the EPA Five Cities Urban Airshed Model Study (Morris et al., 1990a,c). These data sets are described in more detail in the following paragraphs.

Philadelphia

The Philadelphia UAM modeling domain consisted of an array of 35 by 35 5 km grids with five vertical layers. The modeling domain includes the 10 county Philadelphia Air Quality Control Region which covers portions of the states of Pennsylvania, New Jersey, and Delaware. The time span of the model simulation covered from midnight to 1800 on 13 July, 1979. Anthropogenic (man-made) emissions for 1994 were created by projecting the 1985 National Acid Precipitation Assessment Program (NAPAP) national inventory to 1994, with mobile source emissions modified for 9 Reid Vapor Pressure gasoline and future year fleet mix using the EPA MOBILE-4 emission program. Biogenic emissions were also included in the 1994 emission scenarios. Further information on the Philadelphia modeling data base is presented by Haney and Braverman (1985) and Morris, Myers, and Carr (1990).

Atlanta

The modeling domain used in the Atlanta UAM application is an array of 40 by 40 4 km grid cells with five vertical layers. The simulation starts at noon on 3 June 1984 and terminates at 1800 on 4 June 1984. Anthropogenic emissions for the 1994 emission scenarios were developed from the 1985 NAPAP emission inventory and MOBILE-4. Biogenic emissions were obtained from the EPA. Further information on the Atlanta UAM modeling data base is presented by Morris and others (1990a,c).

3 MODIFICATION OF MOBILE4 DETERIORATION RATES

The results of the Ethyl fleet testing program with HiTEC 3000 were incorporated into the mobile source emission inventories used for Urban Airshed Model simulations. It was assumed that only light duty gas vehicles would use gasoline with the HiTEC 3000 additive, and that only exhaust mass emissions rates were affected. The Ethyl fleet test data were used to alter the basic exhaust emission rates which were used to generate the mobile emission inventories. Ratios of the new emission rates to those used to develop the base case inventories were then used to adjust the total mobile emissions. The basic exhaust emission rates adjusted were those produced by the MOBILE4 emission factor model.

MOBILE4 (EPA, 1989) is a model developed by the EPA to estimate motor vehicle emission factors for hydrocarbons, carbon monoxide, and nitrogen oxides. Exhaust, evaporative, running loss, and refueling emission factors are estimated for several categories of vehicles (e.g., light, medium, and heavy duty cars and trucks). The model calculates these emission factors for a composite fleet composed of 20 model years of vehicles, based upon national averages of registration distributions, mileage accumulations, and emission rate equations by vehicle age. The primary user inputs for MOBILE4 are calendar year, maximum and minimum ambient temperatures, and vehicle speed, and Reid Vapor Pressure, although options are available for the user to provide alternate inputs for many of the parameters built into the model. Emission factors estimated by MOBILE4 are then used in conjunction with vehicle miles travelled (VMT) estimates for an area to produce the actual mobile emissions inventories which are used in air quality modeling exercises.

The light duty gas vehicle (LDGV) exhaust emission rate equations, which are built into MOBILE4, take the form of a zero mileage level (ZML), which is a grams per mile emission rate for new vehicles, and deterioration rates (DR), which express the change (i.e., increase) in the zero mileage level per 10,000 miles accumulated by the

vehicle. Two deterioration rates are calculated for 1981 and later LDGV HC and CO emissions. The first (labelled DET in MOBILE4) is for mileage accumulated up to 50,000 miles, and the second (DET2) is for subsequent mileage accumulation. Only one deterioration rate is used for LDGV NO_x emissions, and pre-1981 vehicle emission rates of HC and CO.

From Ethyl's fleet testing data, zero mileage levels and deterioration rates analogous to those in MOBILE4 were calculated using simple linear regression. For each of the eight model groups in Ethyl's test fleet simple linear regression lines were fit to the test fleet data before 50,000 miles (including the tests at 50,000 miles before the component changes) and to data after 55,000 miles separately for clear-fuel and HiTEC 3000 vehicles. From these model-specific regressions, the weighted averages were calculated for the zero mileage level, and the pre- and post-50,000 mile deterioration rates. The weighted average results for the clear-fuel cars predict substantially lower emissions than those predicted by MOBILE4. The differences are shown in Figures 3-1 to 3-3, which show predicted emission rates from MOBILE4, from Ethyl's clear-fuel vehicles, and from Ethyl's HiTEC 3000 vehicles for 1988 model year automobiles.

The differences between MOBILE4 and Ethyl's clear-fuel emission rates were to be expected, as Ethyl's clear-fuel vehicles are very well maintained, while the MOBILE4 results are based on an in-use vehicle population. EPA's in-use population is divided into four emitter categories -- passing, marginal, high, and super emitters. The vehicles in Ethyl's fleet represent passing and marginal emitters only; none fall into the MOBILE4 definitions of high or super emitters, which have a disproportionately large influence on the predicted emission rates.

Because the deterioration rates from Ethyl's fleet are so different from those in MOBILE4, a procedure had to be developed to add HiTEC 3000 effects to the emission rates as predicted by MOBILE4. HiTEC 3000 zero mileage levels and deterioration rates for the twenty model years of LDGVs represented in the mobile inventory were calculated by applying percentage changes at the fitted values at 0, 50,000, and 75,000 miles to the MOBILE4 values. Thus, for each model year 1975 through 1994 LDGV, the following calculations were performed using these fitted values. Subscripts HT and EEE refer to HiTEC 3000 and Howell EEE fleet data,

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HC (g/mile)

FIGURE 3-1. Comparison of hydrocarbon deterioriation rates from MOBILE 4, Ethyl's clear-fuel vehicles, and Ethyl's HiTEC 3000 fuel vehicles.
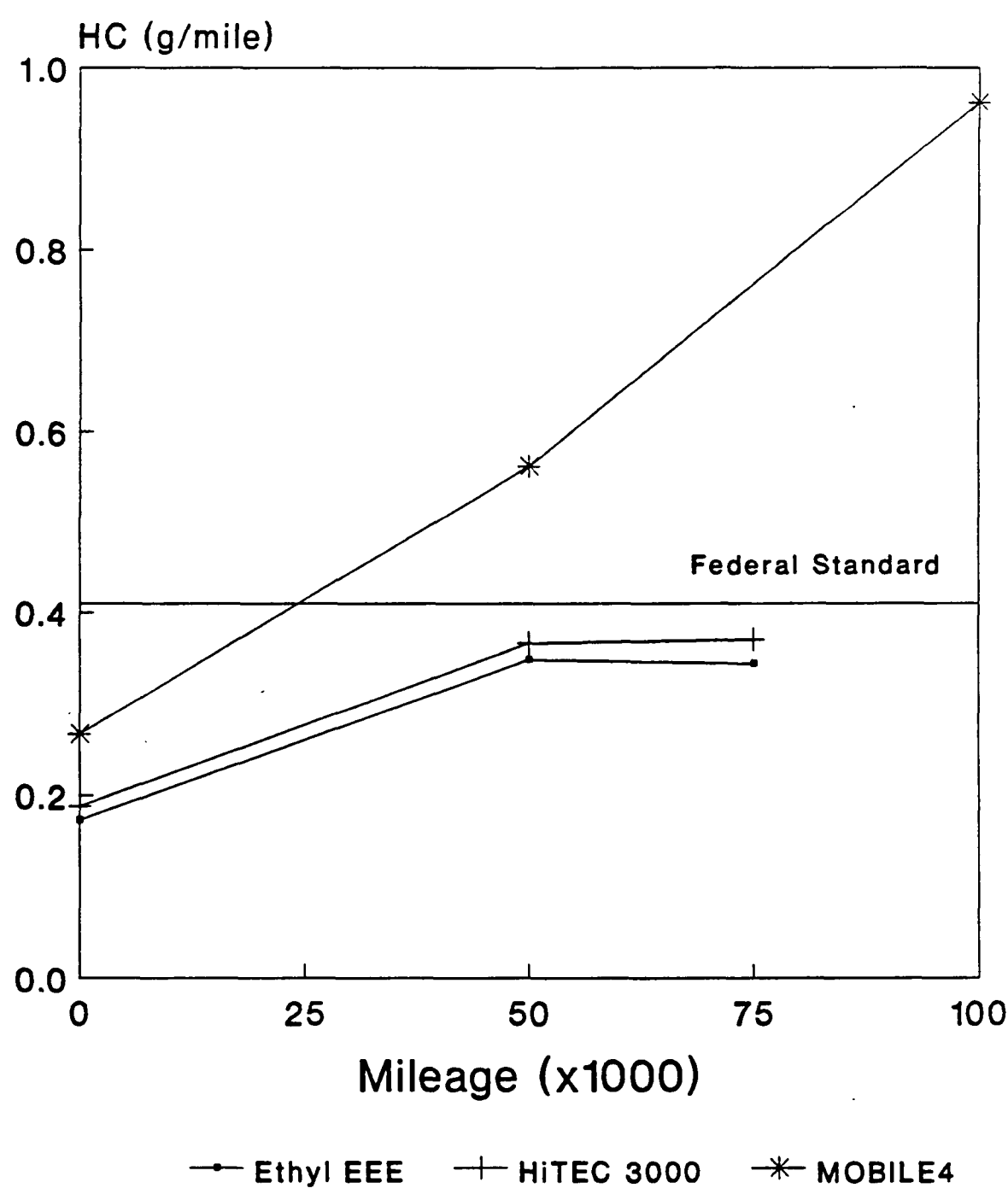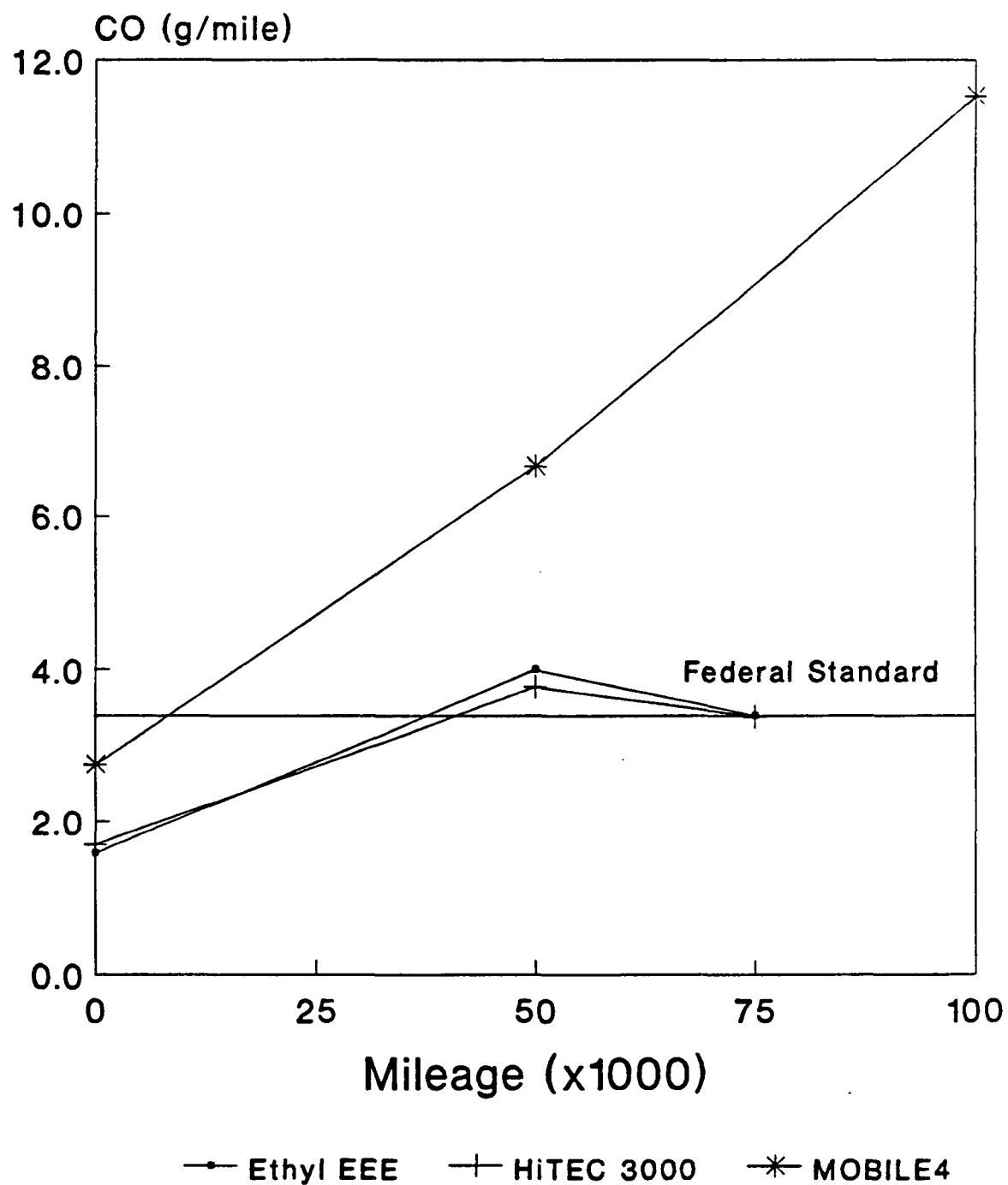
FIGURE 3-2. Comparison of carbon monoxide deterioration rates from MOBILE 4, Ethyl's clear-fuel vehicles, and Ethyl's HiTEC 3000 fuel vehicles.
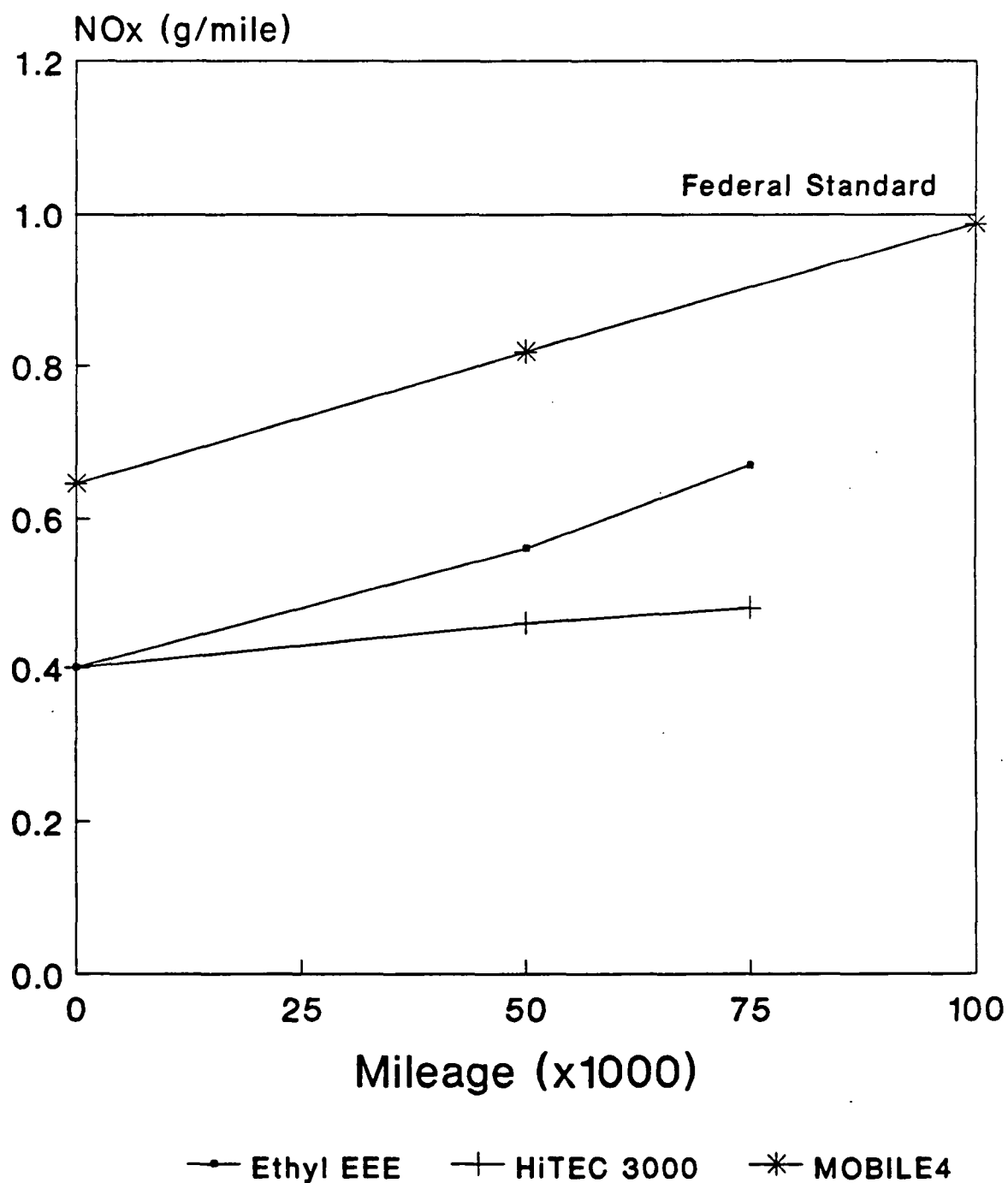
FIGURE 3-3. Comparison of nitrogen oxides deterioration rates from
MOBILE 4, Ethyl's clear-fuel vehicles, and Ethyl's HiTEC 3000 fuel vehicles.

respectively; subscript M4 refers to MOBILE4; and subscript M4HT refers to MOBILE4+HiTEC 3000.

$$ZML_{M4HT} = ZML_{M4} * (ZML_{HT}/ZML_{EEE})$$

$$50K_{M4HT} = 50K_{M4} * (50K_{HT}/50K_{EEE})$$

$$DET_{M4HT} = (50K_{M4HT} - ZML_{M4HT})/5$$

$$75K_{M4HT} = 75K_{M4} * (75K_{HT}/75K_{EEE})$$

$$DET2_{M4HT} = (75K_{M4HT} - 50K_{M4HT})/2.5$$

As an example, we provide the calculations for the HiTEC 3000 1988 LDGV basic exhaust emission rate for CO. From MOBILE4, the 1988 CO zero mileage level is 2.757 g/mi, the 0 to 50,000 mile deterioration rate is 0.780 g/mi/10k miles, and the post-50,000 mile deterioration rate is 0.973 g/mi/10k miles. These parameters give a MOBILE4 50,000 mile emission level of 6.66 g/mi, and a 75,000 mile emission level of 9.09 g/mi. From the regression analyses of Ethyl's fleet testing data described in Appendix 2A, the (predicted) zero mileage levels for clear-fuel and HiTEC 3000, respectively, are 1.584 and 1.694 g/mi; the (predicted) 50,000 mile emission rates are 4.000 and 3.781 g/mi/10k mi; and the (predicted) 75,000 mile emission rates are 3.403 and 3.377 g/mi/10K mi. The HiTEC 3000 emission rates (g/mi) corresponding to 0, 50,000, and 75,000 miles are calculated by applying percentage changes from clear-fuel to HiTEC 3000 as

$$ZML_{M4HT} = 2.757 * (1.694/1.584)$$
$$= 2.947,$$

$$50K_{M4HT} = 6.66 * (3.781/4.000)$$
$$= 6.29, \text{ and}$$

$$75K_{M4HT} = 9.09 * (3.377/3.403)$$
$$= 9.02.$$

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The 0 to 50,000 mile deterioration rate corresponding to HiTEC 3000 is then calculated as the slope of the line between the predicted zero mileage level and the 50,000 mile emission rate, and the post-50,000 mile deterioration rate is calculated as the slope of the line between the predicted 50,000 and 75,000 mile emission rates (units are g/mi/10K mi):

$$DET_{M4HT} = (6.29 - 2.947)/5$$
$$= 0.669, \text{ and}$$

$$DET2_{M4HT} = (9.02 - 6.29)/2.5$$
$$= 1.091.$$

Since HiTEC 3000 would not be introduced into the LDGV fleet until the year 1991, we then weighted the MOBILE4+HiTEC 3000 zero mileage levels and deterioration rates, by model year, with the MOBILE4 zero mileage levels and deterioration rates, to reflect the fraction of each model year's total mileage by 1994 which would have been accumulated with the HiTEC 3000 additive. This was accomplished with a simple linear ratio of mileage accumulated after the introduction of HiTEC 3000 in 1991 to total mileage accumulated by each model year by 1994. The standard mileage accumulation rates by vehicle age are built into the MOBILE4 model. From these accumulation rates, the mileage accummulated by each model year on fuel without HiTEC 3000 can be calculated with the assumption that HiTEC 3000 is introduced in 1991. The standard mileage accumulation by model year and the calculated mileage accumulated before the 1991 introduction of HiTEC 3000 are shown for each model year in Table 3-1.

As an example, we provide the calculation of the weighted NO_x zero mileage level and deterioration rates for 1988 LDGV. For a 1988 model year vehicle, 37,263 miles would have been accumulated on gasoline without the additive. We accounted for the effects of this in the basic emission rates input to MOBILE4 by using the default MOBILE4 zero mileage level of 2.757 g/mi, and we weighted the 0 to 50,000 mile deterioration rate as follows, using the deterioration rates calculated above:

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TABLE 3-1. Mileage accumulations by model year.

Model Year	Total Mileage From MOBILE4	Mileage Accumulated Without HiTEC 3000
1975	162793	142919
1976	158231	137221
1977	153408	131197
1978	148309	124828
1979	142919	118095
1980	137221	110978
1981	131197	103454
1982	124828	95500
1983	118095	87091
1984	110978	78202
1985	103454	68804
1986	95500	58869
1987	87091	48366
1988	78202	37263
1989	68804	25526
1990	58869	13118
1991	48366	0
1992	37263	0
1993	25526	0
1994	13118	0

$$DET_{wt'd} = DET_{M4} * (37263/50000) + DET_{M4HT} * (1-37263/50000)$$
$$= 0.752 \text{ g/mi per } 10,000 \text{ miles}$$

The post-50,000 mile deterioration rate used was the $DET2_{M4HT}$ calculated above, 1.091 g/mi per 10,000 miles, since all mileage past 50,000 miles would be accumulated with the addition of HiTEC 3000.

The resulting weighted MOBILE4+HiTEC 3000 zero mileage levels and deterioration rates for all twenty model years used to produce the new mobile inventories are listed in Tables 3-2 to 3-4 for HC, CO, and NO_x, respectively, along with the default MOBILE4 values for comparison.

These new zero mileage levels and deterioration rates were then input into MOBILE4 to generate emission factors for LDGVs which reflected the use of the HiTEC 3000 fuel additive. The ratio between these new emission factors and those used to generate the base case LDGV emissions was used as an adjustment factor on the LDGV emissions in the mobile source inventory to produce a HiTEC 3000 mobile source inventory.

Total emissions of HC, CO, and NO_x for the 1994 base case and HiTEC 3000 inventories are shown in Tables 3-5 and 3-6 for Atlanta and Philadelphia, respectively. (In these tables THC has been expressed on the basis of kilograms methane per day, rather than on the basis of the actual molecular weights of each of its components.) Because of differences in ambient temperature, inspection and maintenance programs, and anti-tampering programs, the percentage effects of HiTEC 3000 differ between the two cities. For all three pollutants in both cities, changes in the total inventory are less than one percent. In Atlanta, the use of HiTEC 3000 results in total inventory reductions of 0.50 percent for NO_x and 0.09 percent for CO, and an increase of 0.09 percent for HC. In Philadelphia, the effects of HiTEC 3000 usage on the total inventory are a reduction of 0.60 percent in NO_x and 0.15 percent in CO, and an increase of 0.12 percent in HC. The effects of these minimal changes in the total emissions inventory on ambient air quality are discussed in Section 5.

TABLE 3-2. Adjusted MOBILE4 basic emission rates for THC.

Model Year	Default MOBILE4			MOBILE4 + HiTEC 3000			Weighted MOBILE4 + HiTEC 3000		
	ZML	DET	DET2	ZML	DET	DET2	ZML	DET	DET2
1975	1.06	0.28	0.28	1.148	0.287	0.287	1.06	0.281	0.281
1976	1.06	0.28	0.28	1.148	0.287	0.287	1.06	0.281	0.281
1977	1.06	0.28	0.28	1.148	0.287	0.287	1.06	0.281	0.281
1978	1.06	0.28	0.28	1.148	0.287	0.287	1.06	0.281	0.281
1979	1.06	0.28	0.28	1.148	0.287	0.287	1.06	0.281	0.281
1980	0.36	0.10	0.10	0.390	0.103	0.103	0.36	0.100	0.100
1981	0.308	0.079	0.108	0.334	0.081	0.123	0.308	0.079	0.113
1982	0.305	0.074	0.101	0.330	0.076	0.116	0.305	0.074	0.107
1983	0.257	0.062	0.085	0.278	0.063	0.097	0.257	0.062	0.091
1984	0.242	0.067	0.088	0.262	0.069	0.101	0.242	0.067	0.095
1985	0.254	0.063	0.084	0.275	0.064	0.096	0.254	0.063	0.092
1986	0.265	0.060	0.081	0.287	0.061	0.093	0.265	0.060	0.091
1987	0.264	0.060	0.081	0.286	0.061	0.093	0.264	0.060	0.093
1988	0.267	0.059	0.080	0.289	0.060	0.092	0.267	0.059	0.092
1989	0.269	0.059	0.079	0.291	0.060	0.091	0.269	0.060	0.091
1990	0.271	0.058	0.078	0.294	0.059	0.090	0.271	0.059	0.090
1991	0.275	0.057	0.077	0.298	0.058	0.089	0.298	0.058	0.089
1992	0.278	0.056	0.076	0.301	0.057	0.088	0.301	0.057	0.088
1993	0.278	0.056	0.076	0.301	0.057	0.088	0.301	0.057	0.088
1994	0.278	0.056	0.076	0.301	0.057	0.088	0.301	0.057	0.088

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TABLE 3-3. Adjusted MOBILE4 basic emission rates for CO.

Model Year	Default MOBILE4			MOBILE4 + HITEC 3000			Weighted MOBILE4 + HITEC 3000		
	ZML	DET	DET2	ZML	DET	DET2	ZML	DET	DET2
1975	17.72	2.46	2.46	18.942	1.888	1.888	17.72	2.390	2.390
1976	17.72	2.46	2.46	18.942	1.888	1.888	17.72	2.384	2.384
1977	17.72	2.46	2.46	18.942	1.888	1.888	17.72	2.377	2.377
1978	17.72	2.46	2.46	18.942	1.888	1.888	17.72	2.369	2.369
1979	17.72	2.46	2.46	18.942	1.888	1.888	17.72	2.361	2.361
1980	6.09	0.73	0.73	6.510	0.540	0.540	6.09	0.694	0.694
1981	3.378	1.147	1.765	3.611	1.001	1.924	3.378	1.147	1.819
1982	3.376	1.079	1.616	3.609	0.937	1.770	3.376	1.079	1.676
1983	2.731	0.760	1.013	2.919	0.651	1.129	2.731	0.760	1.066
1984	2.432	0.840	1.052	2.600	0.734	1.169	2.432	0.840	1.115
1985	2.611	0.803	1.014	2.791	0.695	1.132	2.611	0.803	1.090
1986	2.764	0.771	0.982	2.955	0.661	1.100	2.764	0.771	1.077
1987	2.720	0.786	0.983	2.908	0.676	1.101	2.720	0.782	1.101
1988	2.757	0.780	0.973	2.947	0.669	1.091	2.757	0.752	1.091
1989	2.785	0.774	0.967	2.977	0.663	1.085	2.785	0.720	1.085
1990	2.813	0.769	0.961	3.007	0.657	1.080	2.813	0.687	1.080
1991	2.870	0.757	0.949	3.068	0.645	1.068	3.068	0.645	1.068
1992	2.915	0.748	0.939	3.116	0.635	1.058	3.116	0.635	1.058
1993	2.915	0.748	0.939	3.116	0.635	1.058	3.116	0.635	1.058
1994	2.915	0.748	0.939	3.116	0.635	1.058	3.116	0.635	1.058

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TABLE 3-4. Adjusted MOBILE4 basic emission rates for NO_x.

Model Year	Default MOBILE4			MOBILE4 + HiTEC 3000			Weighted MOBILE4 + HiTEC 3000		
	ZML	DET	DET2	ZML	DET	DET2	ZML	DET	DET2
1975	2.44	0.04	0.04	2.428	-0.057	-0.057	2.44	0.028	0.028
1976	2.44	0.04	0.04	2.428	-0.057	-0.057	2.44	0.027	0.027
1977	1.79	0.11	0.11	1.781	0.024	0.024	1.79	0.098	0.098
1978	1.79	0.11	0.11	1.781	0.024	0.024	1.79	0.096	0.096
1979	1.79	0.11	0.11	1.781	0.024	0.024	1.79	0.095	0.095
1980	1.50	0.07	0.07	1.493	0.002	0.002	1.50	0.057	0.057
1981	0.651	0.067	0.067	0.648	0.031	0.031	0.651	0.067	0.067
1982	0.633	0.071	0.071	0.630	0.035	0.035	0.633	0.071	0.071
1983	0.632	0.039	0.039	0.629	0.009	0.009	0.632	0.039	0.039
1984	0.663	0.035	0.035	0.660	0.004	0.004	0.663	0.035	0.035
1985	0.651	0.035	0.035	0.648	0.005	0.005	0.651	0.035	0.035
1986	0.641	0.035	0.035	0.638	0.005	0.005	0.641	0.035	0.035
1987	0.647	0.034	0.034	0.644	0.004	0.004	0.647	0.033	0.033
1988	0.646	0.034	0.034	0.643	0.004	0.004	0.646	0.026	0.026
1989	0.644	0.034	0.034	0.641	0.004	0.004	0.644	0.019	0.019
1990	0.642	0.034	0.034	0.639	0.004	0.004	0.642	0.012	0.012
1991	0.638	0.034	0.034	0.635	0.004	0.004	0.635	0.004	0.004
1992	0.635	0.034	0.034	0.632	0.004	0.004	0.632	0.004	0.004
1993	0.635	0.034	0.034	0.632	0.004	0.004	0.632	0.004	0.004
1994	0.635	0.034	0.034	0.632	0.004	0.004	0.632	0.004	0.004

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TABLE 3-5a.   1994 Atlanta THC (1000 kg/day)

Source Category	Base Case	% of Total	HiTEC 3000	% of Total	% HiTEC 3000 change from Base
LDGV exhaust	61.6	2.88	63.2	2.96	2.60
Total mobile	248.0	11.61	250.0	11.69	0.81
Stationary area	405.0	18.96	405.0	18.94	0
Total area	653.0	30.57	655.0	30.64	0.31
Biogenics	1390.0	65.26	1390.0	65.20	0
Total	2136.0		2138.0		0.09

TABLE 3-5b.   1994 Atlanta CO Emissions (1000 kg/day)

Source Category	Base Case	% of Total	HiTEC 3000	% of Total	% HiTEC 3000 change from Base
LDGV exhaust	433.0	39.08	431.0	38.93	-0.46
Total mobile	700.1	63.19	698.3	63.08	-0.26
Stationary area	368.9	33.29	368.9	33.32	0
Total area	1069.0	96.48	1067.1	96.40	-0.18
Biogenics	0	0	0	0	0
Total	1108.0		1107.0		-0.09

TABLE 3-5c.   1994 Atlanta NO_x Emissions (1000 kg/day)

Source Category	Base Case	% of Total	HiTEC 3000	% of Total	% HiTEC 3000 change from Base
LDGV exhaust	75.7	10.26	72.0	9.80	-4.89
Total mobile	207.4	28.10	203.7	27.74	-1.78
Stationary area	68.6	9.29	68.6	9.34	0
Total area	276.0	37.39	272.3	37.08	-1.34
Biogenics	0	0	0	0	0
Total	738.1		734.4		-0.50

TABLE 3-6a.   1994 Philadelphia THC Emissions (1000 kg/day)

Source Category	Base Case	% of Total	HiTEC 3000	% of Total	% HiTEC 3000 change from Base
LDGV exhaust	122.0	4.42	124.0	4.49	1.64
Total mobile	445.0	16.13	448.0	16.22	0.67
Stationary area	1390.0	50.38	1390.0	50.32	0
Total area	1835.0	66.51	1838.0	66.54	0.16
Biogenics	572.0	20.73	572.0	20.71	0
Total	2758.9		2762.2		0.12

TABLE 3-6b.   1994 Philadelphia CO Emissions (1000 kg/day)

Source Category	Base Case	% of Total	HiTEC 3000	% of Total	% HiTEC 3000 change from Base
LDGV exhaust	927.0	33.47	922.0	33.35	-0.54
Total mobile	1359.0	49.07	1354.4	48.98	-0.34
Stationary area	854.8	30.87	854.8	30.91	0
Total area	2213.8	79.94	2209.3	79.90	-0.21
Biogenics		0	0	0	0
Total	2769.3		2765.0		-0.15

TABLE 3-6c.   1994 Philadelphia NO_x Emissions (1000 kg/day)

Source Category	Base Case	% of Total	HiTEC 3000	% of Total	% HiTEC 3000 change from Base
LDGV exhaust	132.0	12.57	126.0	12.07	-4.55
Total mobile	324.7	30.91	318.5	30.50	-1.92
Stationary area	162.4	15.46	162.4	15.55	0
Total area	487.1	46.37	480.9	46.05	-1.28
Biogenics	0	0	0	0	0
Total	1050.4		1044.1		-0.60

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4 ANALYSIS OF SPECIATION DATA FOR HiTEC 3000

As part of Ethyl Corporation's program to determine whether the use of HiTEC 3000 causes or contributes to the failure of emission control systems to meet applicable emission standards, two refinery linear programming models representing 45% of U.S. gasoline production were run by Turner, Mason, and Co. (TM&C) (see Appendix 6, Attachment 6-1). In their report, TM&C concluded, among other things, that the use of HiTEC 3000 would reduce the aromatics content of gasoline by about one percent (from 31% to 30%). This represents over a three percent reduction in total gasoline aromatics.

This potential reduction in gasoline aromatics is of particular interest in light of a number of studies that have been published over the last year. These studies indicate that an increase in the aromatic concentration of gasoline leads to an increase in all three regulated exhaust emissions (HC, CO, NO_x) (Piel, 1989; Colucci, 1989, Appendix 9). Conversely, the results of these studies suggest that "reducing the aromatic content of gasoline can make significant improvements in the cars' exhaust emissions relative to their ozone forming tendency" (Piel, 1989).

The suggestions made in the above referenced studies are of particular interest to Ethyl's waiver application because of the results reported by TM&C. By test design, 24 vehicles in Ethyl's waiver fleet were fueled with Howell EEE certification gasoline while 24 vehicles were fueled with Howell EEE containing 0.03125 grams Mn/gallon as HiTEC 3000. Because HiTEC 3000 is an antiknock compound, the octane quality of the two fuels differ. While this difference has no impact on the operation of an automobile, the composition of a gasoline blended with HiTEC 3000 would be different from that blended without the product as indicated by the TM&C study.

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ETHYL CORPORATION SPECIATION PROGRAM

To further evaluate the potential HiTEC 3000 effects on HC emissions, Ethyl retained Southwest Research Institute (SwRI) to conduct chemical speciation testing on the regulated exhaust emissions from two of the waiver fleet vehicles. In particular, two vehicles from model group F were removed from the mileage accumulation program in Detroit and transported to SwRI for this speciation analysis.

In the speciation testing, two sets of fuels with the same octane quality were used. In one set of fuels, Howell EEE with either HiTEC 3000 or aromatics was blended to produce equivalent octane numbers. In the second set, a commercial gasoline was blended again to an equal octane with either HiTEC 3000 or aromatics. For both sets of fuels, mileage was accumulated so that any deteriorative effect caused by either the increase in aromatics or the use of HiTEC 3000 could be measured. Emissions testing was conducted for exhaust emissions only and followed the Federal Test Procedure. A complete description of the speciation program is contained in Appendix 4.

SPECIATION PROGRAM RESULTS

The speciation program provided speciation data using several types of base fuels including Howell EEE and commercial unleaded regular gasoline, the fuels relevant to this analysis. HiTEC 3000, at 0.03125 grams Mn/gallon, was blended with each of the base fuels. Then aromatics, as xylene, were blended with each of the base fuels so that the octane matched the HiTEC 3000 blended fuel. Two 1988 model F cars (car codes F3 and F5) from the Ethyl fleet testing program were used with the four fuels studied: Howell EEE with aromatics; Howell EEE with HiTEC 3000; commercial fuel with aromatics; and commercial fuel with HiTEC 3000. The speciation test results for the two 1988 model F cars were analyzed and processed for air quality modeling of the effect of the HiTEC 3000 fuel additive on HC emissions from motor vehicles. The tests for fuels with added HiTEC 3000 were conducted with car F3, whereas, tests using car F5 involved Howell EEE and the commercial fuel with added aromatics (see Appendix 4 for details). Results for four

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tests for each of the four fuels were transmitted by SWRI as Lotus 123 worksheets, each of which contained two tests for a single fuel at the accumulted mile mark. The worksheets contained the test data generated by SWRI for each of the 3 operating modes, i.e., bag 1 is cold start, bag 2 is hot stabilized and bag 3 is hot start. This data was analyzed to determine the reactivity of each blend of fuel.

Speciation and Reactivity

Urban ozone formation from its VOC and NO_x precursors depends on the mass emissions rates and the distribution of species within the VOC and NO_x categories. For NO_x the speciation is fairly simple, being mostly nitric oxide (NO), with 5 to 10 percent nitrogen dioxide (NO_2) plus some trace quantities of other compounds such as nitrous acid (HONO). For the speciation of VOC the situation is very complex, hundreds of organic species with a wide diversity of atmospheric photochemical reactivities.

Much of the reactivity towards ozone formation from vehicular exhaust VOC emissions stems from the combined effects of the fuel and engine design on the combustion process and the emissions control devices used; the rest of VOC reactivity can be attributed to unburnt fuel. The use of any fuel additive that affects octane can be expected to affect primarily the combustion process and secondarily the control devices. For additives with substantial oxygen content, such as MTBE or ethanol, the effect on control devices may be more important in the short term. For additives such as HiTEC 3000 the long term impacts on mass emissions rates due to effects on the control devices was a central focus of the present project, however, the reactivity effects on short term fuel changes was also studied.

The impact of VOC emissions depends on the combined effects of mass emissions, reactive fraction of those emissions, and the speciation profile of the reactive fraction. The first two effects are easy to compare between tests of fuel additives or other parameters which might affect emissions. However, the impact of ozone formation from changes in species profile is very complex. The use of a photochemical grid model is one way of evaluating changes in species profile, but the

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expense of such modeling is so great that all effects are usually included at once. That is, the mass emissions and reactive fraction effects on VOC, NO_x and CO are included at the same time so that the impact due solely to changes in species profile are rarely easy to identify.

For this study two methods were used to evaluate the impact of the species profile changes due to HiTEC 3000: a weighted hydroxyl radical (OH) rate constant method and a three-dimensional photochemical grid model. The weighted OH rate constant method provides an average rate constant per carbon atom for reaction with the hydroxyl radical species (OH). This method can give an indication of the relative reactivities of different fuel mixtures. The photochemical grid model approach gives the actual ozone formation due to the changes in emission mass rates as well as speciation. The results from the photochemical grid modeling are discussed in Chapter 5.

Reaction of Volatile Organic Compounds (VOC) with OH is generally the rate-controlling critical step in urban ozone formation; the rate of this reaction is the product of OH concentration, VOC concentration and the rate constant. This rate constant varys widely with the particular VOC species involved. For example, butane has a per carbon rate constant of about 1,000 $ppmC^{-1}min^{-1}$, while isoprene has a per carbon rate constant of 28,400 $ppmC^{-1}min^{-1}$; butane takes several days to react, while isoprene reacts in a few hours. However, the OH rate constant method does not account for the products of the reaction which often have significantly different effects on ozone formation. Typically, olefins make less ozone than their OH rate constants might imply; aldehydes, especially formaldehyde, typically lead to more urban ozone formation than their OH rate constants might imply.

Table 4-1 summarizes the results comparing mass emissions, reactive fractions and reactivity factors from the Ethyl speciation program. The overall impacts on urban ozone expected from the use of HiTEC 3000 using just these results (i.e., ignoring NO_x and CO effects) are related to the triple products of mass emissions, reactive fractions and reactivity factors. Using the results for the average of the tests we find that using HiTEC 3000 as a fuel additive results in a 22 and 18 percent reduction in the ozone formation potential of exhaust emissions from the fuel as compared to using the more common aromatics fuel additive for the, respectively, commercial

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TABLE 4-1. Speciation results for 1988 model F cars exhaust emissions.

	FTP (mg/mi)	VOC/THC Ratio	Average OH Rate Constant $(ppmC^{-1} min^{-1})$	OH Reactivity Ozone Formation Potential
Commercial fuel				
plus aromatics (1,000 miles)	542	0.681	3233	
plus HiTEC 3000 (1,000 miles)	510	0.646	3144	
plus aromatics (2,000 miles)	569	0.757	3135	
plus HiTEC 3000 (2,000 miles)	479	0.674	2960	
plus aromatics (average)	556	0.719	3184	1,272,849
plus HiTEC 3000 (average)	494	0.660	3052	995,074
Howell EEE fuel				
plus aromatics (500 miles)	566	0.744	2575	
plus HiTEC 3000 (500 miles)	476	0.704	2464	
plus aromatics (1,000 miles)	573	0.761	2771	
plus HiTEC 3000 (1,000 miles)	550	0.725	2624	
plus aromatics (average)	570	0.752	2673	1,145,755
plus HiTEC 3000 (average)	513	0.714	2544	931,821

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fuel and Howell EEE base fuel. Note that the only data from the Ethyl speciation program used to define UAM emission scenarios was the data on the composition of the THC. The mass emission amounts from the speciation program were not used since it was felt that the Ethyl fleet testing program provided a much better and robust data set for estimating the effect of HiTEC 3000 on changes in mass emissions.

As can be derived from Table 4-1, of the 22 percent difference in ozone formation potential between commercial fuel plus aromatics and commercial fuel plus HiTEC 3000 approximately 10 percent is due to differences in mass THC emission rates, approximately 8 percent is due to differences in VOC-to-THC ratios, and about 4 percent is due to differences in the average OH rate constant of the mixture. Thus, even though HiTEC 3000 produces 1 to 3 percent more THC from exhaust emissions (see Table 3-5 and 3-6), since THC emissions from HiTEC 3000 vehicles have approximately 8 percent more nonreactive portion, then exhaust emissions from vehicles powered by gasoline with the HiTEC 3000 additive will produce 5 to 7 percent less VOC emissions.

UTILIZATION OF THE SPECIATION DATA IN THE UAM

In order to simulate the effect of HiTEC 3000 on air quality using the Urban Airshed Model (UAM) light duty gas vehicle (LDGV) mass emission rates for total hydrocarbons (THC), nitrogen oxides (NO_x), and carbon monoxide (CO) are needed along with the composition of the THC into Carbon Bond IV chemical mechanism species. The LDGV mass emission rates were derived from the Ethyl fleet testing program data using the procedures described in chapter 3. In this section we describe how the Ethyl Corporation speciation program data were used to specify the composition of the THC emissions for LDGV exhaust and evaporative emissions.

The most representative speciation data from the speciation program is the speciation data from the 1988 cars using commercial fuel plus aromatics, for the base case emissions scenario, and the commercial fuel plus HiTEC 3000, for the HiTEC 3000 emissions scenario. These data were used to develop LDGV exhaust chemical speciation profile (profile number 1203). The speciation profile for LDGV

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evaporative emissions (profile number 1204) in the HiTEC 3000 emission scenario was based on the Air Emission Speciation Profile (AESM) for this category adjusted for 9 RVP following the procedures recommended by the EPA (see Morris et al., 1989). For the base case (i.e. commercial fuel plus aromatics) allowances to the AESM evaporative profile were made to account for the presence of larger amounts of aromatics.

Exhaust Profiles

For each mode of operation, cold start, hot stabilized and hot start, the initial two tests and the second two tests taken after an additional 1000 miles were combined to generate the FTP weighted exhaust profile for each fuel. For each bag, each species was summed across the four tests and all species summed. The factors used to generate the FTP weighted profiles are the factors used by MOBILE4. The three factors are 0.206, 0.521 and 0.273 for bags 1, 2, and 3, respectively. The weighted fraction for each individual chemical compound in the profiles is calculated by summing the 3 weighted bag total for each species and dividing by the sum of the weighted total of all species for each bag. The final normalized FTP weight fraction exhaust profile for AESM, commercial fuel with HiTEC 3000 and commercial fuel with added aromatics are shown in Table 4-2.

Evaporative Profiles

The speciation program did not include lab speciation of the evaporative components of the blended fuels. To reflect the change in fuel composition, two evaporative profiles were generated by modification of the AESM evaporative profile 1204. These were adjusting the default profile to represent a Reid Vapor Pressure (RVP) of 9 and adjusting the default profile to reflect added aromatics.

As per EPA guidance (see Morris et al., 1989), the weight fractions that represent RVP 9 are:

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TABLE 4-2

Speciation profiles for exhaust emissions (profile number 1203) with 108 species
(units are wt fractions normalized to 1)

Saroad code	Chemical Compound	AESM	HITEC	Aromatic
======	==========================	======	=======	========
43135	C10 PARAFFINS	0.0019	--	--
43136	C9 PARAFFIN	0.0	0.0010	0.0
43201	METHANE	0.1097	0.2910	0.2380
43202	ETHANE	0.0179	0.0680	0.0520
43203	ETHYLENE	0.0841	0.0450	0.0510
43204	PROPANE	0.0	0.0040	0.0040
43205	PROPENE	0.0288	0.0190	0.0200
43206	ACETYLENE	0.0225	0.0020	0.0020
43208	PROPADIENE	0.0013	--	--
43209	METHYLACETYLENE (PRO	0.0017	--	--
43211	3-METHYL-1-PENTENE	0.0	0.0	0.0
43212	N-BUTANE	0.0381	0.0720	0.0800
43213	BUTENE	0.0	0.0030	0.0040
43214	ISOBUTANE	0.0062	0.0090	0.0080
43215	ISOBUTYLENE	0.0141	0.0060	0.0070
43216	TRANS-2-BUTENE	0.0	0.0020	0.0030
43217	CIS-2-BUTENE	0.0046	0.0020	0.0030
43218	1,3-BUTADIENE	0.0067	0.0020	0.0020
43220	N-PENTANE	0.0160	0.0450	0.0420
43221	ISOPENTANE	0.0351	0.1130	0.1070
43223	3-METHYL-1-BUTENE	0.0018	--	--
43224	1-PENTENE	0.0019	0.0	0.0
43226	TRANS-2-PENTENE	0.0034	0.0020	0.0020
43227	CIS-2-PENTENE	0.0020	0.0010	0.0
43228	2-METHYL-2-BUTENE	0.0051	0.0070	0.0070
43229	2-METHYLPENTANE	0.0127	0.0160	0.0150
43230	3-METHYLPENTANE	0.0086	0.0200	0.0190
43231	HEXANE	0.0067	0.0090	0.0090
43232	HEPTANE	0.0053	0.0020	0.0030
43233	OCTANE	0.0030	0.0010	0.0020
43234	2,3-DIMETHYL-1-BUTEN	0.0	0.0	0.0
43235	NONANE	0.0025	0.0010	0.0010
43238	N-DECANE	0.0020	0.0040	0.0010
43241	N-UNDECANE	0.0060	0.0	0.0
43242	CYCLOPENTANE	0.0	0.0	0.0
43243	ISOPRENE	0.0017	0.0010	0.0010
43245	1-HEXENE	0.0022	--	--
43247	2,4-DIMETHYLPENTANE	0.0053	0.0020	0.0030
43248	CYCLOHEXANE	0.0162	0.0010	0.0
43250	2,2,4-TRIMETHYLPENTA	0.0195	0.0250	0.0270
43252	2,3,4-TRIMETHYLPENTA	0.0011	0.0080	0.0090
43261	METHYLCYCLOHEXANE	0.0047	0.0030	0.0030
43262	METHYLCYCLOPENTANE	0.0061	0.0120	0.0140
43263	2-METHYLHEXANE	0.0	--	--
43270	3-METHYL-TRANS-2-PEN	0.0	--	--
43272	METHYLCYCLOPENTENE	0.0002	0.0	0.0010
43273	CYCLOHEXENE	0.0	0.0	0.0
43274	2,3-DIMETHYLPENTANE	0.0125	--	--
43276	2,3-DIMETHYLBUTANE	0.0053	0.0090	0.0070
43277	2,4-DIMETHYLHEXANE	0.0	--	--
43278	2,5-DIMETHYLHEXANE	0.0063	--	--

TABLE 4-2 Concluded

Code	Compound				
43279	2-ETHYL-1-BUTENE	0.0	—	—	—
43280	2,3,3-TRIMETHYLPENTA	0.0110	0.0120	0.0110	—
43281	1-BUTYNE	0.0	—	—	—
43282	2-BUTYNE	0.0	—	—	—
43283	CIS-3-HEXENE	0.0	—	—	—
43284	2-METHYL-2-PENTENE	0.0023	—	—	—
43285	2-HEXENE	0.0008	—	—	—
43286	DIMETHYLHEXENE	0.0013	—	—	—
43287	2,2-DIMETHYLHEXANE	0.0007	—	—	—
43290	2,3-DIMETHYLHEXANE	0.0	—	—	—
43291	2,2-DIMETHYLBUTANE	0.0071	—	0.0010	—
43292	CYCLOPENTENE	0.0027	0.0	0.0	0.0
43295	3-METHYLHEXANE	0.0092	0.0080	0.0090	—
43296	2-METHYLHEXANE	0.0022	—	—	—
43297	4-METHYLHEPTANE	0.0052	—	—	—
43298	3-METHYLHEPTANE	0.0036	—	0.0040	0.0040
43299	1-METHYLCYCLOHEXENE	0.0	—	—	—
43502	FORMALDEHYDE	0.0142	0.0110	0.0110	0.0110
43503	ACETALDEHYDE	0.0049	0.0040	0.0040	0.0040
43504	PROPIONALDEHYDE	0.0005	0.0	0.0	0.0
43505	ACROLEIN (PROPENAL)	0.0015	0.0	0.0	0.0
43515	CROTONALDEHYDE	0.0007	0.0	0.0	0.0
45110	C10 AROMATIC	0.0265	—	—	—
45201	BENZENE	0.0162	0.0150	0.0230	—
45202	TOLUENE	0.0572	0.0200	0.0240	—
45203	ETHYLBENZENE	0.0088	0.0040	0.0100	—
45204	O-XYLENE	0.0176	0.0070	0.0150	—
45205	M-XYLENE	0.0	—	—	—
45206	P-XYLENE	0.0287	—	—	—
45207	1,3,5-TRIMETHYLBENZE	0.0221	0.0020	0.0040	—
45208	1,2,4-TRIMETHYLBENZE	0.0290	0.0090	0.0090	—
45209	N-PROPYLBENZENE	0.0056	0.0010	0.0010	—
45216	SEC-BUTYLBENZENE	0.0017	0.0030	0.0	—
45217	1,2-DIETHYLBENZENE	0.0067	0.0	0.0	—
45218	M-DIETHYLBENZENE	0.0057	0.0030	0.0010	—
45225	1,2,3-TRIMETHYLBENZE	0.0081	—	—	—
45501	BENZALDEHYDE	0.0024	0.0010	0.0010	—
90002	2,3,5-TRIMETHYLHEXAN	0.0011	0.0	0.0	—
90003	2,4-DIMETHYLHEPTANE	0.0013	0.0010	0.0	—
90004	3,5-DIMETHYLHEPTANE	0.0	—	—	—
90005	2,5-DIMETHYLHEPTANE	0.0	—	—	—
90006	2,3-DIMETHYLHEPTANE	0.0	0.0030	0.0010	—
90007	4-METHYL-1-PENTENE	0.0025	0.0	0.0	—
90008	2-METHYLOCTANE	0.0002	0.0	0.0	—
90009	2,4,5-TRIMETHYLHEPTA	0.0045	—	—	—
90042	TRANS-3-HEXENE	0.0020	—	—	—
98033	2,2,5-TRIMETHYLHEXAN	0.0048	0.0020	0.0030	—
98044	INDANE	0.0054	0.0	0.0010	—
99910	2,4-DIMETHYLOCTANE	0.0010	—	—	—
99911	3,4-DIMETHYLOCTANE	0.0096	—	—	—
99912	1-METHYL-3-ETHYLBENZ	0.0125	—	—	—
99913	1-METHYL-2-ETHYLBENZ	0.0026	—	—	—
99915	ISOBUTYLBENZENE	0.0049	—	—	—
99916	1-METHYL-3-N-PROPYLB	0.0039	0.0	0.0	—
99917	1-METHYL-3-ISOPROPYL	0.0051	—	—	—
99918	2-METHYLDECANE	0.0132	0.0010	0.0010	—
99999	UNIDENTIFIED	0.0908	—	0.0010	0.0020

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43212	Butane	0.210
43214	Isobutane	0.060
43220	n-Pentane	0.040
43221	Isopentane	0.130

Only the weight fraction for butane in the default AESM profile needed to be adjusted to 0.210 from 0.2834. The profile was then renormalized.

The adjustment for the added aromatics was more complicated. To determine a reasonable factor 5% more aromatics were added to the AESM speciation profile for summer liquid blend fuel (profile 1014) and then renormalized this profile. From this the percent change in the added aromatic was calculated to be 5.008%. This percent change was applied to the same aromatic in the 1204 profile and then the profile was renormalized. The resulting new evaporative profiles are shown in Table 4-3.

UAM EMISSION SCENARIOS

The development of UAM emission inventories for 1994 Philadelphia and Atlanta involves several steps, one of which involves the modification of LDGV to reflect the changes in emissions due to the use of HiTEC 3000. However, a UAM emission inventory requires detailed information concerning the locations, types, mass rates, and composition of emissions from all source categories. In the following paragraphs we first discuss the treatment of emissions from LDGV for the 1994 base case and 1994 HiTEC 3000 emission scenarios and then, briefly, discuss the treatment of emissions from other source categories.

Emissions from Light Duty Gas Vehicles

The UAM requires THC emissions to be specified in terms of Carbon Bond IV (CB-IV) chemical species. The CB-IV chemical species for THC are: olefins (OLE), paraffins (PAR), toluene (TOL), xylene (XYL), formaldehyde (FORM), other higher molecular weight aldehydes (ALD2), ethylene (ETH), and isoprene (ISOP). Each of the individual hydrocarbon species listed in Tables 4-2 and 4-3 are split into CB-IV

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TABLE 4-3

Speciation profiles for evaporative emissions (profile number 1204)
with 108 species (units are wt fractions normalized to 1)

Saroad code	Chemical Compound	RVP 9	Aromatic
======	========================	======	======
43135	C10 PARAFFINS	0.0010	0.0009
43136	C9 PARAFFIN	0.0	0.0
43201	METHANE	0.0004	0.0004
43202	ETHANE	0.0003	0.0003
43203	ETHYLENE	0.0003	0.0003
43204	PROPANE	0.0166	0.0154
43205	PROPENE	0.0	0.0
43206	ACETYLENE	0.0001	0.0001
43208	PROPADIENE	0.0002	0.0002
43209	METHYLACETYLENE (PRO	0.0	0.0
43211	3-METHYL-1-PENTENE	0.0	0.0
43212	N-BUTANE	0.2265	0.2830
43213	BUTENE	0.0	0.0
43214	ISOBUTANE	0.0708	0.0656
43215	ISOBUTYLENE	0.0093	0.0086
43216	TRANS-2-BUTENE	0.0	0.0
43217	CIS-2-BUTENE	0.0087	0.0081
43218	1,3-BUTADIENE	0.0	0.0
43220	N-PENTANE	0.0504	0.0467
43221	ISOPENTANE	0.1466	0.1358
43223	3-METHYL-1-BUTENE	0.0019	0.0018
43224	1-PENTENE	0.0067	0.0062
43226	TRANS-2-PENTENE	0.0120	0.0111
43227	CIS-2-PENTENE	0.0122	0.0113
43228	2-METHYL-2-BUTENE	0.0080	0.0074
43229	2-METHYLPENTANE	0.0246	0.0228
43230	3-METHYLPENTANE	0.0126	0.0117
43231	HEXANE	0.0078	0.0072
43232	HEPTANE	0.0056	0.0052
43233	OCTANE	0.0026	0.0024
43234	2,3-DIMETHYL-1-BUTEN	0.0	0.0
43235	NONANE	0.0013	0.0012
43238	N-DECANE	0.0022	0.0020
43241	N-UNDECANE	0.0010	0.0009
43242	CYCLOPENTANE	0.0	0.0
43243	ISOPRENE	0.0	0.0
43245	1-HEXENE	0.0042	0.0039
43247	2,4-DIMETHYLPENTANE	0.0064	0.0059
43248	CYCLOHEXANE	0.0072	0.0067
43250	2,2,4-TRIMETHYLPENTA	0.0064	0.0059
43252	2,3,4-TRIMETHYLPENTA	0.0064	0.0059
43261	METHYLCYCLOHEXANE	0.0036	0.0033
43262	METHYLCYCLOPENTANE	0.0091	0.0084
43263	2-METHYLHEXANE	0.0	0.0
43270	3-METHYL-TRANS-2-PEN	0.0	0.0
43272	METHYLCYCLOPENTENE	0.0008	0.0007
43273	CYCLOHEXENE	0.0	0.0
43274	2,3-DIMETHYLPENTANE	0.0111	0.0103
43276	2,3-DIMETHYLBUTANE	0.0112	0.0104
43277	2,4-DIMETHYLHEXANE	0.0	0.0
43278	2,5-DIMETHYLHEXANE	0.0052	0.0048

TABLE 4-3 Concluded

Code	Species		
43279	2-ETHYL-1-BUTENE	0.0	0.0
43280	2,3,3-TRIMETHYLPENTA	0.0044	0.0041
43281	1-BUTYNE	0.0	0.0
43282	2-BUTYNE	0.0	0.0
43283	CIS-3-HEXENE	0.0069	0.0064
43284	2-METHYL-2-PENTENE	0.0009	0.0008
43285	2-HEXENE	0.0005	0.0005
43286	DIMETHYLHEXENE	0.0005	0.0005
43287	2,2-DIMETHYLHEXANE	0.0	0.0
43290	2,3-DIMETHYLHEXANE	0.0181	0.0168
43291	2,2-DIMETHYLBUTANE	0.0022	0.0020
43292	3-METHYLPENTENE	0.0083	0.0077
43295	CYCLOPENTENE	0.0022	0.0020
43296	2-METHYLHEPTANE	0.0024	0.0022
43297	4-METHYLHEPTANE	0.0011	0.0010
43298	3-METHYLHEPTANE	0.0038	0.0035
43299	1-METHYLCYCLOHEXENE	0.0	0.0
43502	FORMALDEHYDE	0.0	0.0
43503	ACETALDEHYDE	0.0	0.0
43504	PROPIONALDEHYDE	0.0	0.0
43505	ACROLEIN (PROPENAL)	0.0	0.0
43515	CROTONALDEHYDE	0.0	0.0
45110	C10 AROMATIC	0.0068	0.0063
45201	BENZENE	0.0072	0.0067
45202	TOLUENE	0.0917	0.0849
45203	ETHYLBENZENE	0.0057	0.0053
45204	O-XYLENE	0.0094	0.0091
45205	M-XYLENE	0.0	0.0
45206	P-XYLENE	0.0228	0.0211
45207	1,3,5-TRIMETHYLBENZE	0.0077	0.0071
45208	1,2,4-TRIMETHYLBENZE	0.0131	0.0121
45209	N-PROPYLBENZENE	0.0039	0.0036
45216	SEC-BUTYLBENZENE	0.0017	0.0016
45217	1,2-DIETHYLBENZENE	0.0014	0.0013
45218	M-DIETHYLBENZENE	0.0014	0.0013
45225	1,2,3-TRIMETHYLBENZE	0.0018	0.0017
45501	BENZALDEHYDE	0.0	0.0
90002	2,3,5-TRIMETHYLHEXAN	0.0008	0.0007
90003	2,4-DIMETHYLHEPTANE	0.0005	0.0005
90004	3,5-DIMETHYLHEPTANE	0.0	0.0
90005	2,5-DIMETHYLHEPTANE	0.0	0.0
90006	2,3-DIMETHYLHEPTANE	0.0	0.0
90007	4-METHYL-1-PENTENE	0.0161	0.0149
90008	2-METHYLOCTANE	0.0	0.0
90009	2,4,5-TRIMETHYLHEPTA	0.0	0.0
90042	TRANS-3-HEXENE	0.0016	0.0015
98033	2,2,5-TRIMETHYLHEXAN	0.0014	0.0013
98044	INDANE	0.0041	0.0038
99910	2,4-DIMETHYLOCTANE	0.0014	0.0013
99911	3,4-DIMETHYLOCTANE	0.0022	0.0020
99912	1-METHYL-3-ETHYLBENZ	0.0043	0.0040
99913	1-METHYL-2-ETHYLBENZ	0.0103	0.0095
99915	ISOBUTYLBENZENE	0.0004	0.0004
99916	1-METHYL-3-N-PROPYLB	0.0003	0.0003
99917	1-METHYL-3-ISOPROPYL	0.0002	0.0002
99918	2-METHYLDECANE	0.0023	0.0021
99999	UNIDENTIFIED	0.0282	0.0261

chemical species based on their chemical composition following EPA guidence (Hogo and Gery 1987). Tables 4-4 and 4-5 give the standard AESM CB-IV splitting factors along with the splitting factors for commercial fuel plus either HiTEC 3000 or aromatics for the, respectively, LDGV exhaust and evaporative THC emissions. The exhaust commercial fuel plus aromatics and evaporative AESM with added aromatics splitting factors are used to define the composition of LDGV THC emissions for the base case emissions scenario. The exhaust HiTEC 3000 and evaporative AESM at 9 RVP splitting factors are used to define the composition of the LDGV THC emissions for the HiTEC 3000 emission scenario. The exhaust and evaporative mass emission rates for LDGV were derived from either standard MOBILE 4 or the modifed MOBILE4 emission program as discussed in Chapter 3 and given in Table 3-5 and 3-6.

The reactive portion of the speciation profiles listed in Table 4-4 and 4-5 is obtained by summing up each of the individual species numbers weighted by carbon atoms (number of carbon atoms in each CB-IV species is: 2-OLE, 1-PAR, 7-TOL, 8-XYL, 1-FORM, 2-ALD2, 2-ETH, and 5-ISOP). Thus for commercial fuel plus HiTEC 3000 exhaust emissions the total reactive portion is 0.04418 moles-Carbon/gm-THC. Thus exhaust emissions from vehicles using commercial fuel plus HiTEC 3000 have approximately 8 percent less reactive components than seen for commercial fuel plus aromatics (0.04848 mole-carbon/g THC).

Definition of the Emission Scenarios

The development of the 1994 emission inventories generally followed the same pro-cedures used for the development of 1995 emission scenarios for the EPA Five Cities Urban Airshed Model Study (Morris et al., 1989, 1990a,b,c; Morris Myers, and Carr 1990; Scheffe and Morris 1990). However, some slight modifications to these proce-dures, as described previously, were made to allow for the inclusion of data from the Ethyl Corporation fleet testing and speciation programs. The following paragraphs briefly describe the emission inventory generation procedures used. The reader is referred to the EPA Five Cities UAM Study reports for further details.

The 1994 base case and HiTEC 3000 emission scenarios for Philadelphia and Atlanta were based on the 1985 National Acid Precipitation Assessment Program (NAPAP) annual emission inventory (Zimmerman et al., 1988). This inventory contains

TABLE 4-4

Carbon-bond IV split factors for exhaust
profile 1203 (units moles/g)

	OLE	PAR	TOL	XYL
AESM standard	0.1492e-02	0.3250e-01	0.9969e-03	0.1259e-02
HITEC 3000	0.8434E-03	0.3245E-01	0.2929E-03	0.3706E-03
Added Aromatics	0.9269E-03	0.3304E-01	0.3704E-03	0.6831E-03

	FORM	ALD2	ETH	ISOP
AESM standard	0.4996e-03	0.6162e-03	0.2998e-02	0.2496e-04
HITEC 3000	0.3806E-03	0.6848E-03	0.1604E-02	0.1468E-04
Added Aromatics	0.3663E-03	0.7276E-03	0.1818E-02	0.1468E-04

TABLE 4-5

Carbon-bond IV split factors for evaporative
profile 1204 (units moles/g)

	OLE	PAR	TOL	XYL
AESM at RVP 9	0.7473e-03	0.5282e-01	0.1147e-02	0.6250e-03
Added Aromatics	0.6922E-03	0.5394E-01	0.1063E-02	0.5821E-03

	FORM	ALD2	ETH	ISOP
AESM standard	0.0000e+00	0.1120e-02	0.1070e-04	0.0000e+00
Added Aromatics	0.0000E+00	0.1035E-02	0.1066E-04	0.0000E+00

information for THC, NO_x, and CO emissions for over a hundred different source categories. Area source emissions are supplied at the county level, whereas point source emissions are given by stacks. Emissions from mobile sources were adjusted from annual values to episodic emission rates by using the MOBILE 4 emission program and the temperatures for the episode in question. The mobile source emissions were then projected from 1985 to 1994 by using estimates of VMT growth supplied by Pechan and Associates (Pechan, 1989). Changes in mobile sources due to fleet turnover and the 9 RVP gasoline assumed in 1994 were incorporated by using the MOBILE 4 emission program.

Emissions from nonmobile sources were projected from 1985 to 1994 using projection factors (Pechan, 1989). These emissions were then speciated following standard EPA guidance (Shareff et al., 1988). Biogenic emissions were based on data developed as part of NAPAP (Lamb et al., 1986, 1987).

The county level area sources are then disaggregated to the UAM grid structure using a known surrogate distribution. For example, emissions from residential heating are disaggregated using population while emissions from limited access roadways (freeways) are disaggregated based on a digitization of freeway systems. THC and NO_x emissions are then speciated using source category specific speciation profiles.

The simulation of emissions from refineries that process HiTEC 3000 performance additive in unleaded gasoline performed by TM&C indicated some changes in refinery NO_x emissions (see Appendix 6, Attachment 6-1). These changes in refinery NO_x emissions were integrated into the HiTEC 3000 emission scenarios for Philadelphia. There were no refineries located in the Atlanta UAM modeling domain. Changes in refinery NO_x emissions when HiTEC 3000 is added to unleaded gasoline in Philadelphia resulted in a 0.03 percent reduction in elevated NO_x emissions over the base case.

Philadelphia

The total THC emissions for Philadelphia given in Table 3-6 were speciated into Carbon Bond IV chemical mechanism hydrocarbon classes using the speciation profiles listed in Table 4-4 and 4-5 for exhaust and evaporative emissions from LDGVs and using AESM speciation profiles (Shareef et al., 1988) for other source categories.

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The resultant total VOC (reported as methane), NO_x, and CO emissions for the Philadelphia 1994 base case and 1994 HiTEC 3000 emission scenario are given in Table 4-6. Note that despite the fact that emissions from LDGV using HiTEC 3000 emit higher amounts of THC (Table 3-6), a larger portion of these emissions are nonreactive (Table 4-4 and 4-5) resulting in less total reactive hydrocarbon (VOC) emissions.

Atlanta

Similar results are seen in the 1994 base case and 1994 HiTEC 3000 emission scenarios for Atlanta (Table 4-7). VOC emissions from LDGVs in the 1994 HiTEC 3000 emissions scenario are less than in the 1994 base case.

Summary

In summary, the following assumptions were used to develop the 1994 base case and HiTEC 3000 emission scenarios for Philadelphia and Atlanta:

Anthropgenic emissions based on the 1985 NAPAP annual national emissions inventory,

Mobile source emissions were adjusted to episodic temperature conditions using the MOBILE 4 emission program,

Biogenic emissions were based on data from NAPAP,

Anthropogenic emissions were projected from 1985 to 1994 using projection factors developed for the EPA,

The HiTEC 3000 emission scenario assumed full penetration of HiTEC 3000 into all LDGV starting in 1991. Emissions from heavy duty gas vehicles, diesel vehicles, and off road vehicles were assumed not to be using HiTEC 3000.

TABLE 4-6a.   1994 Philadelphia VOC Emissions (1000 kg/day)
(constant octane).

Source Category	Base Case	% of Total	HiTEC 3000	% of Total	% HiTEC 3000 change from Base
LDGV exhaust	84.1	3.55	78.3	3.32	-6.90
Total mobile	391.7	16.54	384.2	16.28	-1.92
Stationary area	1082.2	45.71	1082.2	45.85	0
Total area	1474.0	62.25	1466.5	62.13	-0.51
Biogenics	572.0	24.16	572.0	24.23	0
Total	2367.9		2360.4		-0.32

TABLE 4-6b.   1994 Philadelphia CO Emissions (1000 kg/day)

Source Category	Base Case	% of Total	HiTEC 3000	% of Total	% HiTEC 3000 change from Base
LDGV exhaust	927.0	33.47	922.0	33.35	-0.54
Total mobile	1359.0	49.07	1354.4	48.98	-0.34
Stationary area	854.8	30.87	854.8	30.91	0
Total area	2213.8	79.94	2209.3	79.90	-0.21
Biogenics		0	0	0	0
Total	2769.3		2765.0		-0.15

TABLE 4-6c.   1994 Philadelphia NO_x Emissions (1000 kg/day)

Source Category	Base Case	% of Total	HiTEC 3000	% of Total	% HiTEC 3000 change from Base
LDGV exhaust	132.0	12.57	126.0	12.07	-4.55
Total mobile	324.7	30.91	318.5	30.50	-1.92
Stationary area	162.4	15.46	162.4	15.55	0
Total area	487.1	46.37	480.9	46.05	-1.28
Biogenics	0	0	0	0	0
Total	1050.4		1044.1		-0.60

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LDGV emissions for the base case are from MOBILE 4 for 1994 assuming 9 RVP fuel and using episodic temperature conditions,

LDGV exhaust mass emissions for the HiTEC 3000 emission scenario are from the modified version of MOBILE 4 that reflects the effect of HiTEC 3000 on deterioration rates as described in Chapter 3. LDGV evaporative mass emissions were based on the standard MOBILE 4.

Speciation of the LDGV exhaust and evaporative THC emissions for the base case was based on the Ethyl speciation program data for commercial fuel plus aromatics, whereas speciation of LDGV THC emissions for the HiTEC 3000 emission scenarios was based on the speciation data for the commercial fuel plus HiTEC 3000.

Sensitivity Tests

Two UAM emission sensitivity tests were also performed for 1994 Philadelphia and Atlanta. The first sensitivity test used mass emission rates as listed in Table 3-5 and 3-6 and the same speciation profiles for the base case and HiTEC 3000 emission scenarios. The AESM exhaust and evaporative (modified for 9 RVP gasoline) profiles as given in Table 4-4 and 4-5 were used with the mass emission rates given in Table 3-5 and 3-6 resulting in the VOC emissions given in Table 4-8 and 4-9. This sensitivity test was designed to determine the sensitivity of the calculated effects of HiTEC 3000 to the Ethyl speciation data by expressing the UAM using the same exhaust and evaporation speciation profiles for the base case and HiTEC 3000 emissions scenarios. It represents a conservative estimate (i.e., tending toward overstatement of any adverse effects) of the effect of HiTEC 3000 on air quality since it is using the same speciation profiles for gasoline of different octanes.

The second sensitivity test eliminated emission from LDGV. The emissions used in this no LDGV emission sensitivity test for Philadelphia and Atlanta are given in Tables 4-10 and 4-11. This sensitivity test is designed to determine the maximum benefit possible by modifying emissions from LDGV. The UAM is exercised with no

TABLE 4-7a.   1994 Atlanta VOC (1000 kg/day) (constant octane).

Source Category	Base Case	% of Total	HiTEC 3000	% of Total	% HiTEC 3000 change from Base
LDGV exhaust	42.6	2.11	39.8	1.97	-6.57
Total mobile	218.4	10.81	214.4	10.63	-1.83
Stationary area	322.0	15.94	322.0	15.98	0
Total area	540.4	26.75	536.4	26.61	-0.74
Biogenics	1394.0	69.01	1394.0	69.15	0
Total	2019.9		2016.0		-0.20

TABLE 4-7b.   1994 Atlanta CO Emissions (1000 kg/day)

Source Category	Base Case	% of Total	HiTEC 3000	% of Total	% HiTEC 3000 change from Base
LDGV exhaust	433.0	39.08	431.0	38.93	-0.46
Total mobile	700.1	63.19	698.3	63.08	-0.26
Stationary area	368.9	33.29	368.9	33.32	0
Total area	1069.0	96.48	1067.1	96.40	-0.18
Biogenics	0	0	0	0	0
Total	1108.0		1107.0		-0.09

TABLE 4-7c.   1994 Atlanta NO_x Emissions (1000 kg/day)

Source Category	Base Case	% of Total	HiTEC 3000	% of Total	% HiTEC 3000 change from Base
LDGV exhaust	75.7	10.26	72.0	9.80	-4.89
Total mobile	207.4	28.10	203.7	27.74	-1.78
Stationary area	68.6	9.29	68.6	9.34	0
Total area	276.0	37.39	272.3	37.08	-1.34
Biogenics	0	0	0	0	0
Total	738.1		734.4		-0.50

TABLE 4-8a.   1994 Philadelphia VOC Emissions (1000 kg/day) for the Speciation Sensitivity Test (different octanes).

Source Category	Sens. Base Case	% of Total	Sens. HiTEC 3000	% of Total	% HiTEC 3000 change from Base
LDGV exhaust	105.0	4.39	107.0	4.47	1.90
Total mobile	417.3	17.43	419.8	17.52	0.59
Stationary area	1082.2	45.21	1082.2	45.17	0
Total area	1499.3	62.64	1502.0	62.69	0.18
Biogenics	572.0	23.90	572.0	23.88	0
Total	2393.5		2396.0		0.10

TABLE 4-8b.   1994 Philadelphia CO Emissions (1000 kg/day)

Source Category	Sens. Base Case	% of Total	Sens. HiTEC 3000	% of Total	% HiTEC 3000 change from Base
LDGV exhaust	927.0	33.47	922.0	33.35	-0.54
Total mobile	1359.0	49.07	1354.4	48.98	-0.34
Stationary area	854.8	30.87	854.8	30.91	0
Total area	2213.8	79.94	2209.3	79.90	-0.21
Biogenics		0	0	0	0
Total	2769.3		2765.0		-0.15

TABLE 4-8c.   1994 Philadelphia NO_x Emissions (1000 kg/day)

Source Category	Sens. Base Case	% of Total	Sens. HiTEC 3000	% of Total	% HiTEC 3000 change from Base
LDGV exhaust	132.0	12.57	126.0	12.07	-4.55
Total mobile	324.7	30.91	318.5	30.50	-1.92
Stationary area	162.4	15.46	162.4	15.55	0
Total area	487.1	46.37	480.9	46.05	-1.28
Biogenics	0	0	0	0	0
Total	1050.4		1044.1		-0.60

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TABLE 4-9a. 1994 Atlanta THC (1000 kg/day) for the Speciation Sensitivity Test (different octane).

Source Category	Sens. Base Case	% of Total	Sens. HiTEC 3000	% of Total	% HiTEC 3000 change from Base
LDGV exhaust	53.1	2.61	54.4	2.67	2.45
Total mobile	232.2	11.42	233.7	11.48	0.64
Stationary area	322.0	15.83	322.0	15.82	0
Total area	554.2	27.25	555.7	27.30	0.28
Biogenics	1394.0	68.54	1394.0	68.49	0
Total	2033.9		2035.3		0.07

TABLE 4-9b. 1994 Atlanta CO Emissions (1000 kg/day)

Source Category	Sens. Base Case	% of Total	Sens. HiTEC 3000	% of Total	% HiTEC 3000 change from Base
LDGV exhaust	433.0	39.08	431.0	38.93	-0.46
Total mobile	700.1	63.19	698.3	63.08	-0.26
Stationary area	368.9	33.29	368.9	33.32	0
Total area	1069.0	96.48	1067.1	96.40	-0.18
Biogenics	0	0	0	0	0
Total	1108.0		1107.0		-0.09

TABLE 4-9c. 1994 Atlanta NO_x Emissions (1000 kg/day)

Source Category	Sens. Base Case	% of Total	Sens. HiTEC 3000	% of Total	% HiTEC 3000 change from Base
LDGV exhaust	75.7	10.26	72.0	9.80	-4.89
Total mobile	207.4	28.10	203.7	27.74	-1.78
Stationary area	68.6	9.29	68.6	9.34	0
Total area	276.0	37.39	272.3	37.08	-1.34
Biogenics	0	0	0	0	0
Total	738.1		734.4		-0.50

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TABLE 4-10a. 1994 Philadelphia VOC Emissions (1000 kg/day) for the no LDGV emission sensitivity test.

Source Category	Base Case	% of Total	No LDGV	% of Total	No LDGV change from Base
LDGV exhaust	84.1	3.55	0		-100.00
Total mobile	391.7	16.54	92.5	4.47	-76.38
Stationary area	1082.2	45.71	1082.2	52.32	0
Total area	1474.0	62.25	1174.7	56.79	-20.31
Biogenics	572.0	24.16	572.0	27.65	0
Total	2367.9		2068.6		-12.63

TABLE 4-10b. 1994 Philadelphia CO Emissions (1000 kg/day)

Source Category	Base Case	% of Total	No LDGV	% of Total	No LDGV change from Base
LDGV exhaust	927.0	33.47	0	0	-100.00
Total mobile	1359.0	49.07	433.6	23.52	-68.09
Stationary area	854.8	30.87	854.8	46.36	0
Total area	2213.8	79.94	1288.4	0	-41.80
Biogenics		0	0		
Total	2769.3		1843.9		-33.42

TABLE 4-10c. 1994 Philadelphia NO_x Emissions (1000 kg/day)

Source Category	Base Case	% of Total	No LDGV	% of Total	No LDGV change from Base
LDGV exhaust	132.0	12.57	0	0	-100.00
Total mobile	324.7	30.91	192.1	20.93	-40.84
Stationary area	162.4	15.46	162.4	17.69	0
Total area	487.1	46.37	354.5	38.62	-27.22
Biogenics	0	0	0	0	0
Total	1050.4		917.8		-12.62

TABLE 4-11a.   1994 Atlanta VOC emissions (1000 kg/day) for the no
LDGV emission sensitivity test.

Source Category	Base Case	% of Total	HiTEC 3000	% of Total	No LDGV change from Base
LDGV exhaust	42.6	2.11	0	0	-100.00
Total mobile	218.4	10.81	61.9	3.31	-71.66
Stationary area	322.0	15.94	322.0	17.22	0
Total area	540.4	26.75	389.9	20.86	-27.85
Biogenics	1394.0	69.01	1394.0	74.57	0
Total	2019.9		1869.4		-7.45

TABLE 4-11b.   1994 Atlanta CO Emissions (1000 kg/day)

Source Category	Base Case	% of Total	HiTEC 3000	% of Total	No LDGV change from Base
LDGV exhaust	433.0	39.08	0	0	-100.00
Total mobile	700.1	63.19	267.3	37.90	-61.82
Stationary area	368.9	33.29	368.9	52.31	0
Total area	1069.0	96.48	666.2	94.46	-37.68
Biogenics	0	0	0	0	0
Total	1108.0		705.2		-36.35

TABLE 4-11c.   1994 Atlanta NO_x Emissions (1000 kg/day)

Source Category	Base Case	% of Total	HiTEC 3000	% of Total	No LDGV change from Base
LDGV exhaust	75.7	10.26	0	0	-100.00
Total mobile	207.4	28.10	131.4	19.85	-36.64
Stationary area	68.6	9.29	68.6	10.36	0
Total area	276.0	37.39	200.0	30.21	-27.54
Biogenics	0	0	0	0	0
Total	738.1		662.1		-10.30

LOGV emissions and the ozone reduction from the base case is compared with the reduction from the use of HiTEC 3000. The effect of HiTEC 3000 on urban air quality can then be put into the context of a percentage elimination or addition of cars from the fleet.

5   URBAN AIRSHED MODEL RESULTS

The Urban Airshed Model (UAM) was exercised for the future year 1994 and two cities, Philadelphia and Atlanta, to estimate the effects of HiTEC 3000 on urban air quality. Mobile source emissions from light duty gas vehicles (LDGV) for Total Hydrocarbons (THC), nitrogen oxides (NO_x), and carbon monoxide (CO) and the year 1994 were developed for the base case and HiTEC 3000 emission scenarios using data from the Ethyl fleet testing program following the procedures given in chapter 3. The speciation of the LDGV evaporative and exhaust THC emissions to the individual reactive Volatile Organic Compounds (VOC) for the base case and HiTEC 3000 emission scenarios were based on the results from the Ethyl speciation program using the analysis of these data given in chapter 4. The results from these UAM simulations offer the best estimate of the effects of HiTEC 3000 on urban air quality for the year 1994 in the cities of Philadelphia and Atlanta. Because of differences in atmospheric reactivities, emission mixes, and meteorological conditions in other cities, there may be slight differences in the absolute effects of HiTEC 3000 across different cities. However, the basic result from this modeling exercise, that HiTEC 3000 will not adversely affect air quality, will not vary across cities. In fact, the modeling exercise reported here has indicated that the effect of HiTEC 3000 on changes in mobile source emissions will have a slight beneficial effect on air quality.

Two sensitivity tests were also carried out for the two cities using the UAM. In the first sensitivity test the same speciation was used for LDGV emissions in the 1994 base case and 1994 HiTEC 3000 emission scenarios. The speciation profiles in this sensitivity test were based on those in the EPA's Air Emission Speciation Manual (AESM) (Shareef et al., 1988), where the AESM evaporative speciation profile was modified to reflect the use of 9 RVP gasoline for both the base case and HiTEC 3000 emission scenarios. Note that this speciation sensitivity test will result in a conservative (i.e., tending to overstate any disbenefits from using HiTEC 3000) estimate of

the effect of HiTEC 3000 because the same speciation is used for fuels with two different octanes. The most common nonvolatile octane enhancer is aromatics, a class of hydrocarbon compounds that not only is very effective at forming ozone but also has been documented to increase emissions from mobile sources (Piel 1989; Colucci 1989). Since HiTEC 3000 will most likely be used as a replacement octane enhancer for aromatics, then using the same speciation profiles results in an overestimate of any adverse effects of HiTEC 3000 on air quality.

The second sensitivity test eliminated emissions from light-duty gas vehicles (LDGV). This no LDGV emissions sensitivity test will provide an estimate of the impact of LDGV emissions on peak ozone concentrations.

EFFECTS OF HITEC 3000 ON OZONE CONCENTRATIONS

The effect of HiTEC 3000 on urban ozone concentrations was analyzed several different ways:

Changes in the peak concentration,

Differences in the patterns of daily maximum ozone concentrations across the region and throughout the day,

Changes in population exposure to ozone concentrations in excess of several threshold values (80, 120, and 160 ppb), and

Differences in the areal extent of ozone concentrations across the region and throughout the day.

Daily Maximum Ozone Concentrations

Figure 5-1a and 5-1b displays isopleths of daily maximum ozone concentrations for the 1994 Phildelphia base case and HiTEC 3000 emissions scenarios, respectively.
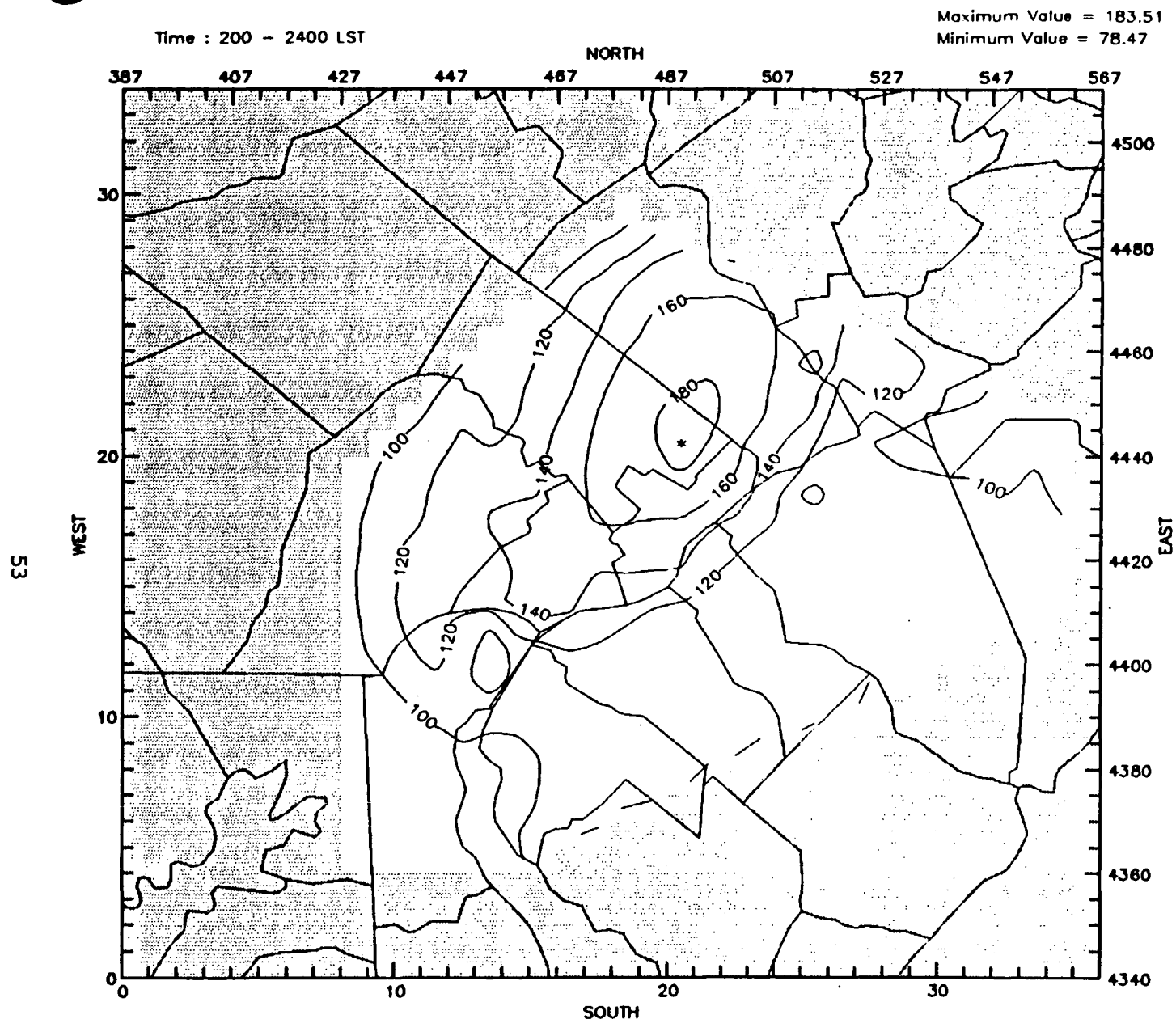
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FIGURE 5-la. Predicted daily maximum ozone concentrations (ppb) in Philadelphia on July 13, 1979 for the 1994 emissions scenario using (1) mass emissions calculated by the standard MOBILE 4 program and (2) hydrocarbon speciation based on commercial fuel plus aromatics

Time : 200 – 2400 LST

Maximum Value = 183.05
Minimum Value = 78.35
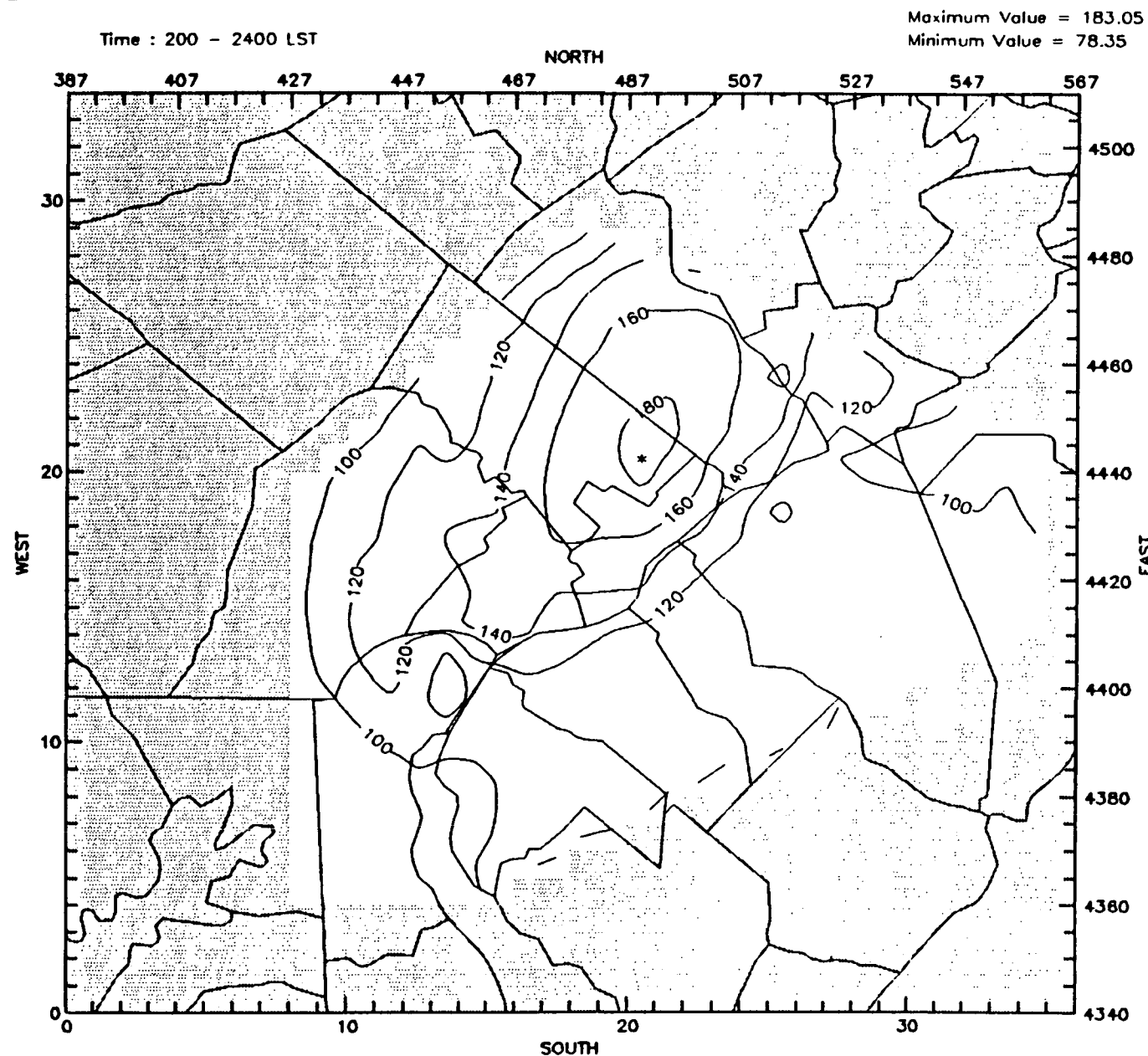
FIGURE 5-1b. Predicted daily maximum ozone concentrations (ppb) in Philadelphia on July 13, 1979 for the 1994 emissions scenario using (1) mass emissions calculated by the MOBILE 4 program modified to reflect the effects of HiTEC 3000 and (2) hydrocarbon speciation based on commercial fuel plus HiTEC 3000.

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P.54
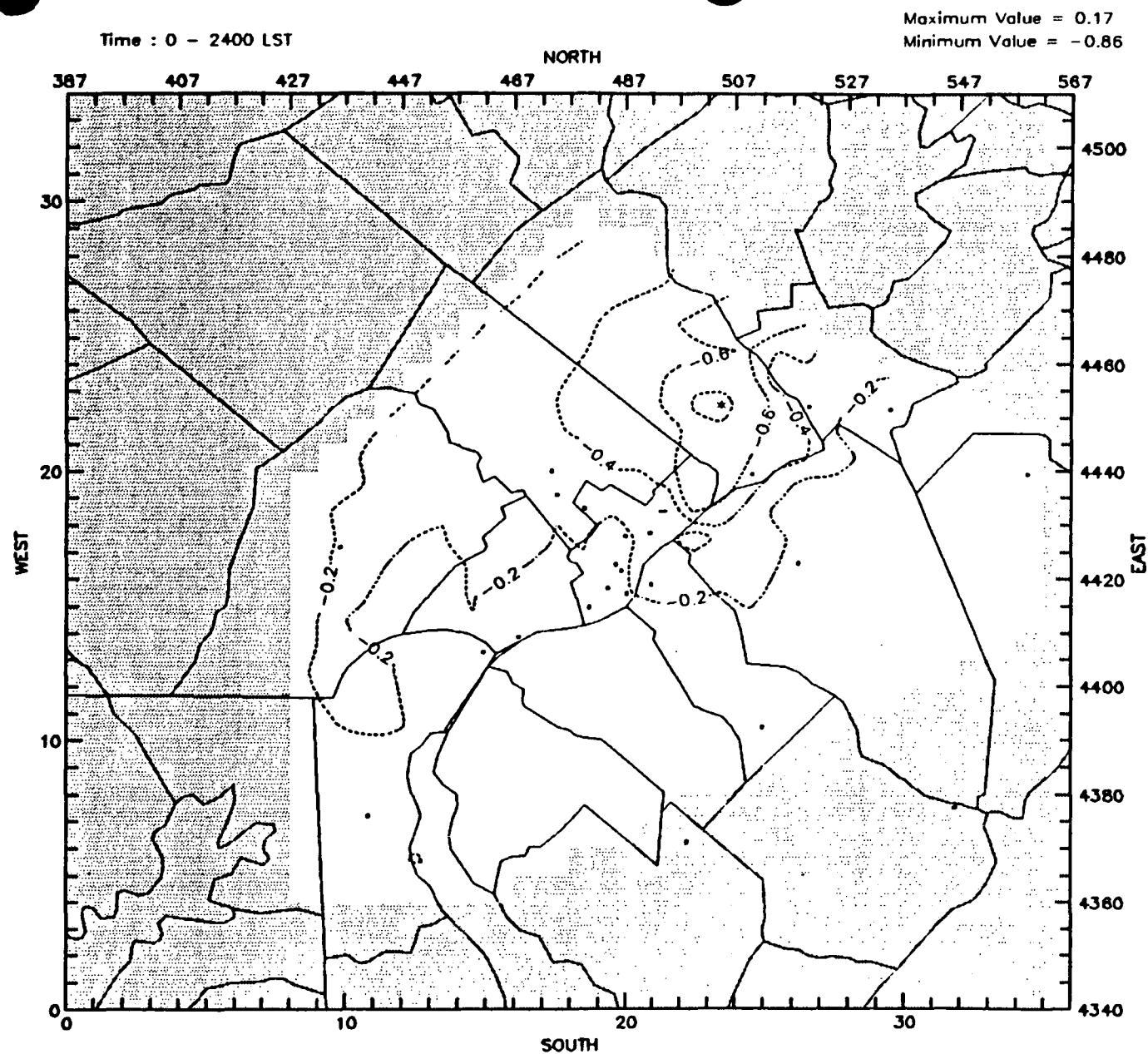
FIGURE 5-1c. Difference in daily maximum ozone concentration (ppb) between predictions shown in Figures 5-1a and b.

Isopleths of the differences in daily maximum ozone concentrations between the base case and HiTEC 3000 emissions scenarios are given in Figure 5-1c. Figure 5-1 indicates that the use of HiTEC 3000 in Philadelphia would result in small decreases in the daily maximum ozone concentrations over most of the region. The maximum decrease in daily maximum ozone concentration due to use of HiTEC 3000 is 0.86 ppb (approximately 0.5 percent) is over a factor of 5 larger than the maximum increase in the daily maximum ozone of 0.17 ppb. The region of decreases of daily maximum ozone concentrations is much larger than the region of increases.

Similar results are seen in Atlanta (Figure 5-2) where the maximum decrease in daily maximum ozone concentrations due to HiTEC 3000 (0.67 ppb) is over 9 times greater than the maximum increase in daily maximum ozone concentrations (0.07 ppb).

The National Ambient Air Quality Standard for ozone is 120 ppb (rounded to the nearest 10 ppb) which is not to be exceeded more than an average of once per year over three years. Thus, in addition to examining how HiTEC 3000 effects daily maximum ozone concentrations across the entire region it is also important to look at how the fuel additive will affect the absolute peak ozone concentrations. Table 5-1 displays the calculated peak ozone concentrations for the 1994 base case and 1994 HiTEC 3000 emission scenarios for Philadelphia and Atlanta. For both cities it is calculated that starting use of HiTEC 3000 in 1991 would results in a decrease in the peak ozone concentration in 1994 of 0.3 percent.

Integrated Measures of the Effect of HiTEC 3000 on Ozone Concentrations

We have developed several integrated measures to determine the effect of HiTEC 3000 on the areal extent of elevated ozone concentrations and the exposure of people to ozone.

Exposure

The first set of measures looks at the total exposure of people to ozone concentrations in excess to several threshold values. In this measure the number of people in a

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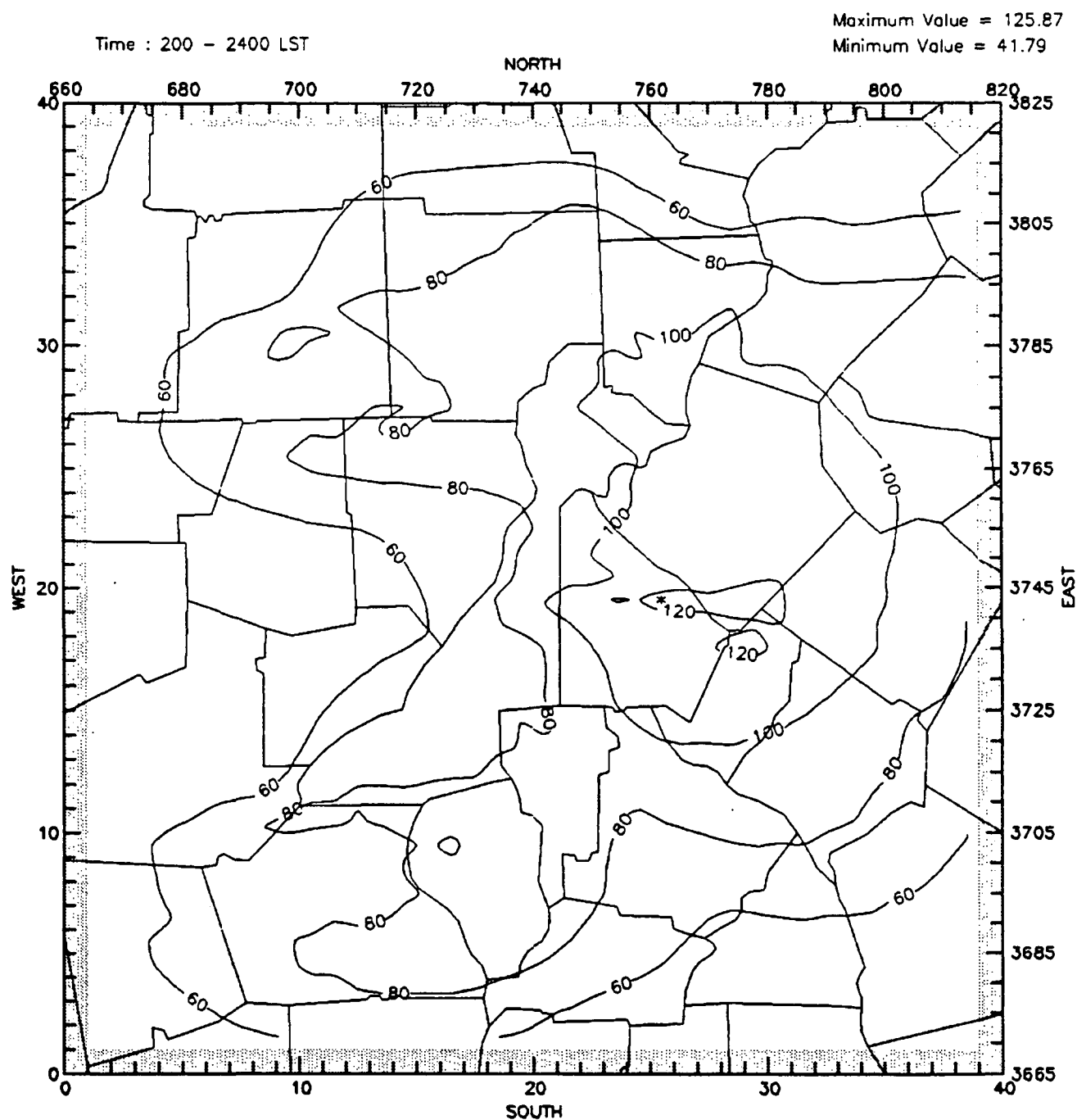
FIGURE 5-2a. Predicted daily maximum ozone concentrations (ppb) in Atlanta on June 4, 1984 for the 1994 emissions scenario using (1) mass emissions calculated by the standard MOBILE 4 program and (2) hydrocarbon speciation based on commercial fuel plus aromatics.
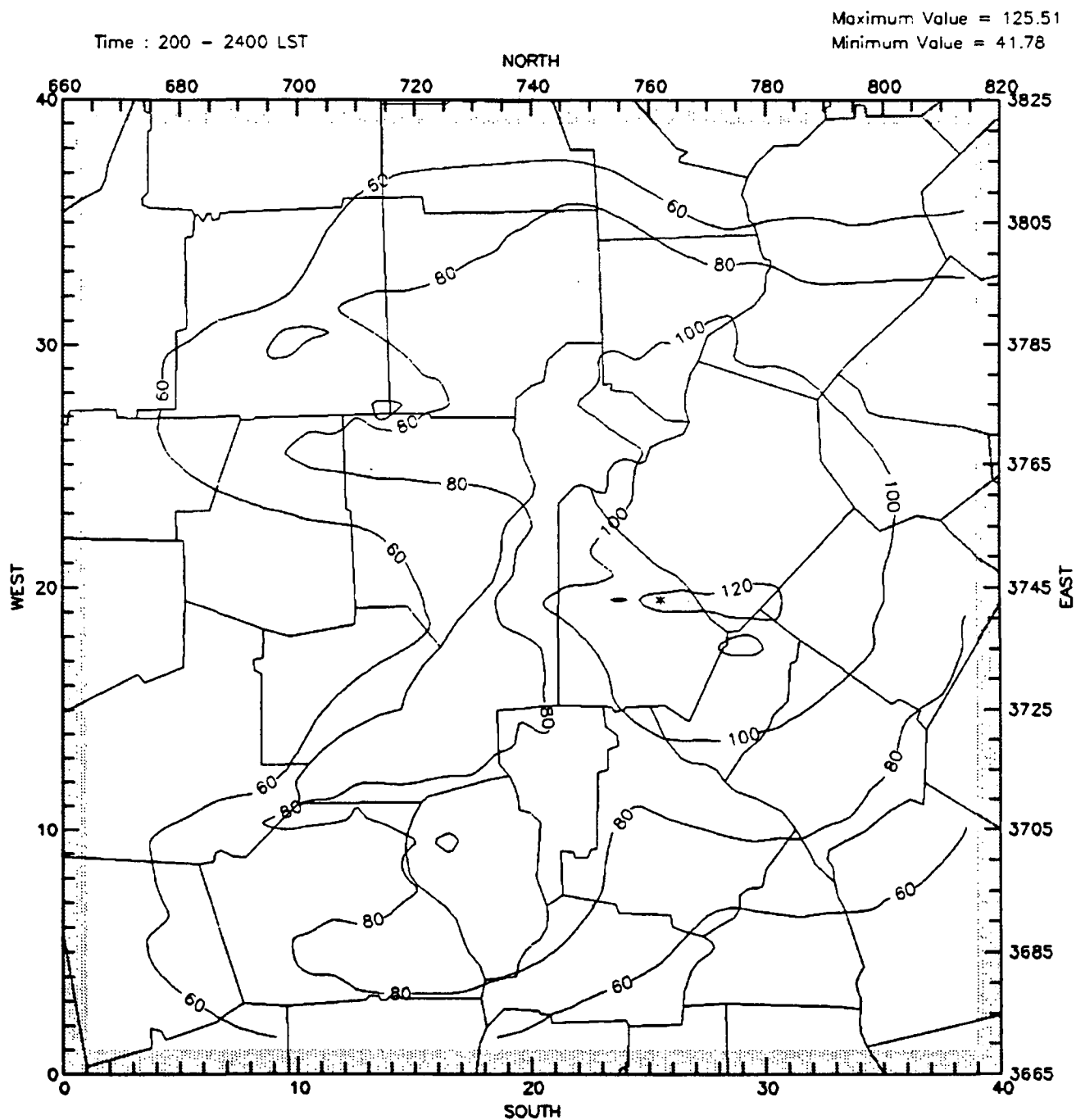
FIGURE 5-2b. Predicted daily maximum ozone concentrations (ppb) in Atlanta on June 4, 1984 for the 1994 emissions scenario using (1) mass emissions calculated by MOBILE 4 program modified to reflect the effects of HiTEC 3000 and (2) hydrocarbon speciation based on commercial fuel plus HiTEC 3000.
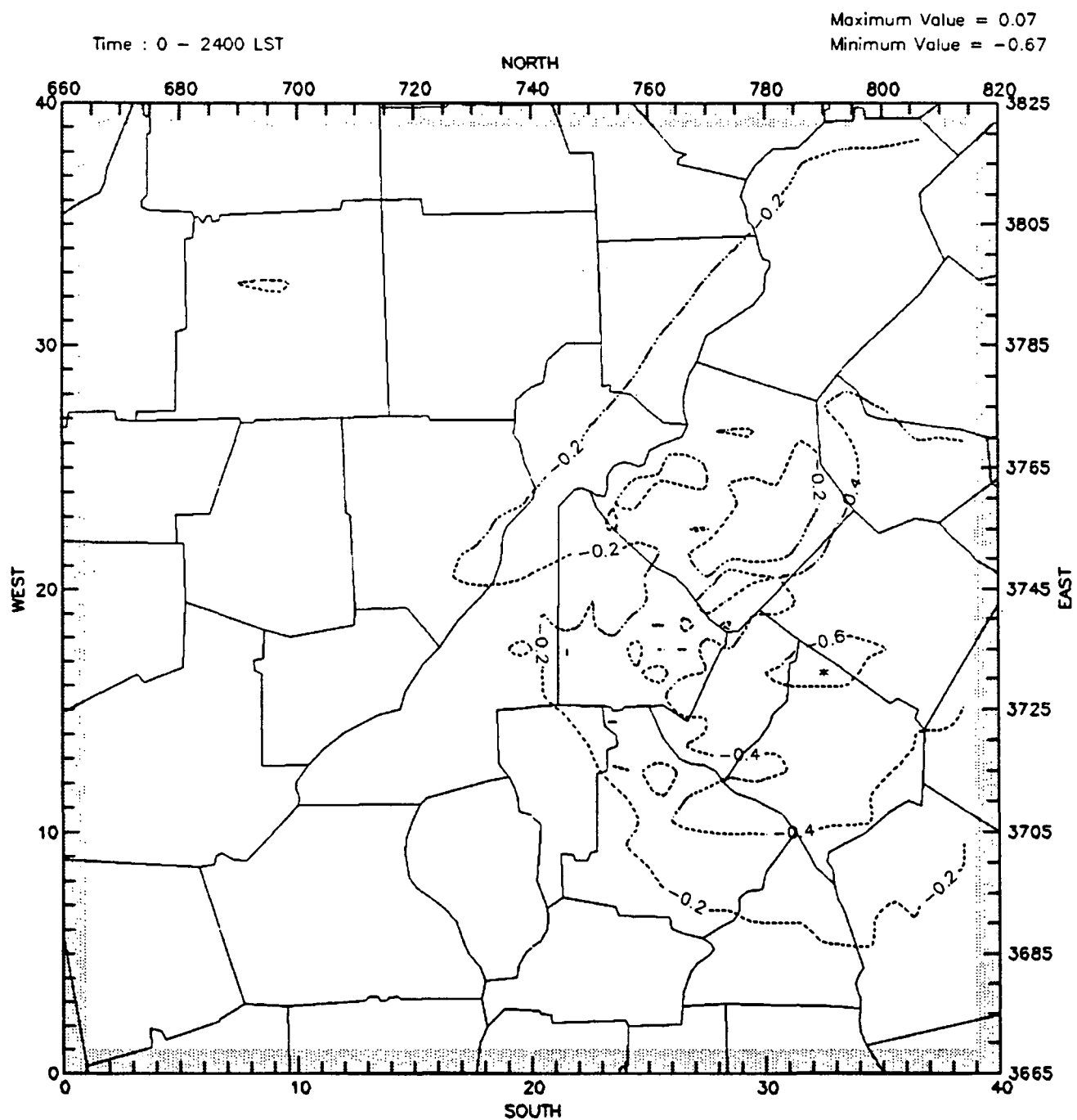
FIGURE 5-2c. Difference in daily maximum ozone concentrations (ppb) between predictions shown in Figures 5-2a and b.

TABLE 5-1. Calculated peak ozone concentrations (ppb) in Philadelphia and Atlanta for the 1994 base case emission scenario using (1) mass emissions calculated by the standard MOBILE 4 program and (2) hydrocarbon speciation based on commercial fuel plus aromatics, and the 1994 HiTEC 3000 emission scenario using (1) mass emissions calculated by the MOBILE 4 program modified to reflect the effects of HiTEC 3000 and (2) hydrocarbon speciation based on commercial fuel plus HiTEC 3000.

| | Peak Ozone Concentration--Constant Octane | | |
	MOBILE 4 Commercial Fuel Plus Aromatics (ppb)	HiTEC 3000 MOBILE 4 Commercial Fuel Plus HiTEC 3000 (ppb)	Percent Change in Peak (%)
Philadelphia	183.5	183.0	-0.3
Atlanta	125.9	125.5	-0.3

grid cell that contains a predicted ozone concentration in excess of the threshold value is summed up over all grid cells and hours of the simulation. Table 5-2 displays these population exposure statistical measures for the 1994 base case and 1994 HiTEC 3000 emission scenarios. For all ozone concentration threshold values and both cities it is calculated that the use of HiTEC 3000 will reduce the population exposure to elevated ozone concentrations. In Philadelphia, it is calculated that approximately 4,000 less people-hours will be exposed to ozone concentrations in excess of the NAAQS (120 ppb) due to the use of HiTEC 3000. Similar results are seen in Atlanta where approximately 400 less people-hours will be exposed to ozone in excess of the NAAQS.

In order to determine the effect of HiTEC 3000 on total population exposure to ozone concentrations for each grid cell and hour we took the differences in ozone concentrations between the 1994 base case and 1994 HiTEC 3000 emission scenarios multiplied by the population in the grid cell summed up over all grid cells and hours of the simulation. The use of HiTEC 3000 in Philadelphia resulted in a reduction in the total exposure to ozone concentrations of 464 ppm-person-hours over the base case. This represents a 0.07 percent reduction in total exposure of people to ozone concentrations for the HiTEC 3000 emission scenario. Again, similar results are seen in Atlanta where 825 ppm-person-hours less exposure to ozone is seen in the HiTEC 3000 emission scenario as compared to the base case. Thus there is a 0.12 percent reduction in total exposure to ozone concentations due to the use of HiTEC 3000 in Atlanta.

Areal Extent

In a manner analogous to the population exposure, measures of the areal extent of ozone concentrations in excess of threshold values was obtained by summing up the area of each grid cell containing an ozone concentration in excess of the threshold value over all grid cells and hours. The results of the area coverage statistics for Philadelphia and Atlanta are displayed in Table 5-3. It is calculated that the use of HiTEC 3000 in 1994 will result in an 0.5 and 11.1 percent reduction in the area

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TABLE 5-2. Effects of HiTEC 3000 on population exposure to ozone concentrations greater than threshold values.

Threshold Ozone Concentrations (ppb)	EPA MOBILE 4 Commercial Fuel Plus Aromatics (1,000 person-hours)	HiTEC 3000 MOBILE Commercial Fuel Plus HiTEC 3000 (1,000 person-hours)	Percent Change (%)
Philadelphia			
> 80	4371	4363	-0.18
> 120	883	879	-0.45
> 160	173	171	-1.16
Atlanta			
> 80	1461	1439	-1.51
> 120	8.7	8.3	-4.60
160	0	0	0

TABLE 5-3. Effects of HiTEC 3000 on the areal extent of ozone concentrations greater than threshold values.

Threshold Ozone Concentrations (ppb)	EPA MOBILE 4 Commercial Fuel Plus Aromatics (1,000 person-hours)	HiTEC 3000 MOBILE 4 Commercial Fuel Plus HiTEC 3000 (1,000 person-hours)	Percent Change (%)
Philadelphia			
> 80	107.9	107.8	-0.09
> 120	19.0	18.9	-0.53
> 160	3.2	3.1	-3.13
Atlanta			
> 80	33.1	32.6	-1.51
> 120	0.18	0.16	-11.11
> 160	0	0	0

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covered by ozone concentrations in excess of the NAAQS for the cities of Philadelphia and Atlanta, respectively. Over all hours there is a reduction of 9.9 (0.06 percent) and 25.8 ppm-km^2-hours (0.12 percent) due to the use of HiTEC 3000 in, respectively, Philadelphia and Atlanta.

EFFECT ON OTHER AIR QUALITY CONCENTRATIONS

Because use of HiTEC 3000 reduces tailpipe NO_x and CO concentrations it should have a beneficial effect of reducing ambient concentration levels of NO_x, NO_2, and CO. Table 5-4 lists the peak CO, NO_2, and NO_x concentrations for several different averaging times calculated in Philadelphia and Atlanta for the 1994 base case and HiTEC 3000 emission scenarios. Note that for Atlanta, the absolute peak NO_2 and NO_x concentrations occur in power plant plumes which is not affected by HiTEC 3000. Thus in Table 5-4 we have reported maximum NO_2 and NO_x concentrations within the urban plume. Isopleths of maximum concentrations and differences in maximum concentrations for CO, NO_2, and NO_x over several averaging times in Philadelphia and Atlanta are given in Figures 5-3 through 5-16 (at end of chapter). For all averaging times the use of HiTEC 3000 results in a reduction in CO, NO_2, and NO_x concentrations. Peak concentrations of these species are reduced from 0.01 to 0.5 percent.

Maximum Possible Atmospheric Manganese Concentrations

The amount of atmospheric manganese concentration due to HiTEC 3000 can be estimated by taking the ratio of tailpipe manganese emissions to tailpipe CO emission rate and applying this ratio to the maximum CO concentration. This scaling of the CO concentrations to the ratio of manganese emissions to CO emissions can be done because CO has very low reactivity. Making the conservative assumption that 40 percent of the CO emissions are from LDGV using HiTEC 3000 (see Table 3-5 and 3-6), mobile source CO emissions are operating at the current standard of 8 gm/mi, and that use of HiTEC 300 produces an average manganese emission rate of 5 µg/mi, which is based on EPA particulate sampling techniques (Appendix 3), we get the following factor to relate CO concentrations to manganese concentrations:

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TABLE 5-4. Calculated peak CO, NO_2, and NO_x concentrations (ppb) in Philadelphia and Atlanta for the 1994 base case emission scenario using (1) mass emissions calculated by the standard MOBILE 4 program and (2) hydrocarbon speciation based on commercial fuel plus aromatics, and the 1994 HiTEC 3000 emission scenario using (1) mass emissions calculated by the MOBILE 4 program modified to reflect the effects of HiTEC 3000 and (2) hydrocarbon speciation based on commercial fuel plus HiTEC 3000.

| | | Peak Concentration--Constant Octane | | |
		EPA MOBILE 4 Commercial Fuel Plus Aromatics (ppb)	HiTEC 3000 MOBILE 4 Commercial Fuel Plus HiTEC 3000 (ppb)	Percent Change in Peak (%)
Philadelphia				
Hourly	CO	1632.61	1632.39	-0.01
8-hour	CO	1338.21	1337.87	-0.03
24-hour	CO	778.04	777.82	-0.03
Hourly	NO_2	70.25	70.23	-0.03
24-hour	NO_2	28.55	28.45	-0.04
Hourly	NO_x	154.90	154.31	-0.39
24-hour	NO_x	51.55	51.31	-0.45
Atlanta				
Hourly	CO	462.99	462.80	-0.04
8-hour	CO	344.75	344.51	-0.07
24-hour	CO	306.19	305.99	-0.07
Hourly	NO_2*	36.68	36.63	-0.14
24-hour	NO_2*	11.62	11.58	-0.34
Hourly	NO_x*	43.87	43.68	-0.43
24-hour	NO_x*	16.11	16.05	-0.37

* Peak concentration within urban plume.

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$$0.40 * 0.000005/8.0 = 2.5 \times 10^{-7}$$

Thus, using the maximum hourly CO concentration for the HiTEC 3000 scenario in Philadelphia of 1633 ppb (note that Atlanta CO concentrations are more than twice as low as those in Philadelphia) we find that a conservative estimate for the maximum hourly manganese concentration due to HiTEC 3000 is approximately 0.0004 ppb, or 0.0009 ug/m3. Thus, use of HiTEC 3000 would produce manganese concentrations that are over one million times smaller than the OSHA standard for manganese fumes of 1,000 ug/m3 (note that the OSHA standard for manganese dust is 5,000 ug/m^3).

Effect of HiTEC 3000 on Benzene Concentrations

Benzene is an extremely toxic pollutant that is a component in gasoline. The primary sources of benzene are mobile source exhaust and evaporative emissions, evaporative emissions from service stations, leakage from the gasoline distribution system, and emissions from refineries. The Ethyl speciation program has indicated that the use of HiTEC 3000 would reduce benzene emissions in LDGV exhaust emissions. As shown in Table 4-2, the weight fraction of benzene emissions in THC exhaust emissions (SAROAD code 45201) in commercial fuel plus HiTEC 3000 (0.015) is approximately 35 percent less than measured in exhaust emissions from commercial fuel plus aromatics (0.0230). The average benzene emissions for commercial fuel plus aromatics and commercial fuel plus HiTEC 3000 were, respectively, 10.9 and 7.0 mg/mile (Appendix 4). HiTEC 3000 will not significantly effect benzene emissions from evaporative emissions.

The percent benzene emissions from LDGV exhaust emissions to the entire urban benzene inventory is uncertain and varies for different urban areas. However, assuming that exhaust LDGV emissions contribute from 10 to 30 percent of the benzene emissions, then the use of HiTEC 3000 would reduce benzene concentrations by approximately 3 to 10 percent.

SPECIATION SENSITIVITY TEST

In the speciation sensitivity test the same exhaust and evaporative speciation pro-
files were used for the standard gasoline and gasoline with HiTEC 3000: that is two
fuels with different octanes. As noted earlier, HiTEC 3000 would be used to enhance
the octane of gasoline as a replacement to aromatics. Since a reduction in aromatics
in gasoline will not only reduce the amount of reactive hydrocarbons but also the
reactivity of the resultant mixture, then this sensitivity test will be a conservative
estimate (i.e., overstate any disbenefits) of the effect of HiTEC 3000 on air quality.

Figure 5-17a and 5-17b display isopleths of the daily maximum ozone concentrations
in Philadelphia for the speciation sensitivity test base case and HiTEC 3000 emission
scenarios. Differences in these daily maximum ozone concentrations are given in
Figure 5-17c. Similar isopleths for Atlanta are given in Figure 5-18. Even with the
conservative estimate of the effect of HiTEC 3000 on mobile source emissions used
in the speciation sensitivity test, the HiTEC 3000 emission scenario in Philadelphia
results in a 0.2 percent reduction in the peak ozone concentration (Table 5-5). In
Atlanta, the speciation sensitivity test results in a 0.2 percent increase in the peak
ozone concentration for the HiTEC 3000 emission scenario.

For Philadelphia the region where the daily maximum ozone concentrations are
reduced due to HiTEC 3000 in the speciation sensitivity test is much larger than the
region of increases (Figure 5-17c). In fact, the region where there are exceedances
of the ozone NAAQS in the speciation sensitivity test base case (Figure 5-17a) is
almost always reduced due to HiTEC 3000. The peak decrease in the daily maximum
ozone due to HiTEC 3000 (0.61 ppb) is almost 50 percent higher than the peak
increase (0.44 ppb).

Even in Atlanta, where it was calculated for the speciation sensitivity scenario that
HiTEC 3000 would increase the peak ozone by 0.2 percent, the region of reductions
in daily maximum ozone concentrations is much larger than the regions of increases
(Figure 5-18c). The maximum reduction in daily maximum ozone concentrations (5.6
ppb) is still larger than the maximum increase (4.1 ppb).

TABLE 5-5. Calculated peak ozone concentrations (ppb) in Philadelphia and Atlanta for 1994 speciation sensitivity tests.

	Peak Ozone Concentration-- Different Octane		
	MOBILE 4 AESM Speciation (ppb)	HiTEC 3000 MOBILE 4 AESM Speciation (ppb)	Percent Change in Peak (%)
Philadelphia	183.8	183.4	-0.2
Atlanta	126.2	126.5	+0.2

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NO LDGV EMISSION SENSITIVITY TEST

In order to determine the maximum environmental benefits possible from modifying emissions from LDGV, a no LDGV emission sensitivity test was carried out using the UAM. All emissions (VOC, NO_x, and CO) from LDGV were eliminated as discussed in chapter 4. Isopleths of the resultant daily maximum ozone concentrations for the no LDGV emissions sensitivity test in Philadelphia and Atlanta are depicted in Figures 5-19 and 5-20. The peak ozone concentrations for the 1994 base case (commercial fuel plus aromatics speciation), 1994 HiTEC 3000 emission scenario (commercial fuel plus HiTEC 3000 speciation), and no LDGV emission sensitivity test are given in Table 5-6. Emissions from LDGV contribute 10.9 ppb (5.9 percent) to the peak ozone concentration in the base case of 183.5 ppb. The use of HiTEC 3000 in LDGV reduces the base case peak ozone concentration in Philadelphia by 0.5 ppb. Based on federal highway statistics it is estimated there will be approximately 3.4 million cars in the Philadelphia CMSA (DOT, 1988). Thus, introducing HiTEC 3000 in 1991 in all LDGV would be equivalent to taking approximately 170,000 (5 percent) light duty gas cars and trucks off the road in Philadelphia in 1994.

Similar results are seen in Atlanta, where the LDGV emissions contribute 5.5 ppb (4.4 percent) to the peak ozone concentration in the base case of 125.9 ppb. Thus assuming that there will be 1.8 million cars in Atlanta in 1994 (DOT, 1988), use of HiTEC 3000 in Atlanta is equivalent to eliminating 129,000 (7.3 percent) automobiles in 1994.

SIGNIFICANCE OF RESULTS

The changes in ozone concentrations due to the use of HiTEC 3000 is sufficiently small that there is some question concerning both the practical significance and the numerical significance (i.e., are the results within the precision of the computer and numerical algorithms used). Concerning the latter, early on in the analysis of the effect of HiTEC 3000 a numerical experiment was performed using Ethyl fleet test data out to 50,000 miles in which the HiTEC 3000 emissions effect was enhanced (using constant speciation, i.e. different octane fuels) by a factor of five and then the resultant calculated changes in ozone concentrations were reduced by a factor of

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TABLE 5-6. Comparison of peak ozone concentrations (ppb) between the 1994 base case, HiTEC 3000 emission scenario, and no LDGV emissions sensitivity test.

| | Peak Ozone Concentrations | | | Ozone Increments | | Percent HiTEC 3000 LDGV Fleet is to Standard LDGV Fleet |
	Base Case (ppb)	HiTEC 3000 Scenario (ppb)	No LDGV Sensitivity Test (ppb)	HiTEC 3000 (ppb)	LDGV Emissions (ppb)	
Philadelphia	183.5	183.0	172.6	-0.5	-10.9	95.4
Atlanta	125.9	125.5	120.4	-0.4	-5.5	92.7

five. The result was the exactly the same ozone impact as was seen without the enhancement and reduction factors. This result indicated that the ozone impacts calculated due to the changes in emissions are valid and above any noise of the precision of the computer and numerical algorithms. Similar numerical experiments with other studies involving small changes in VOC emissions (e.g., underarm sprays and bakeries) has indicated that peak ozone changes calculated by the UAM(CB-IV) on the SAI TRACE 7/300 computer in excess of 0.05 ppb are above any numerical noise. The lower limit of this precision is not known at this time.

Although the calculated effect of HiTEC 3000 on ozone concentrations is a real calculated effect, it is very doubtful that if could be observed using routinely available ozone monitors and current monitoring networks. Concerning the practical significance of the calculated effect on ozone concentrations, it is difficult to attribute the ozone attainment problem to any one source or category of sources. Any one small source can perform simulations that indicate that they are not contributing greatly to a violation of the ozone NAAQS. However, EPA policy is to reduce emissions from many sources to achieve attainment of the ozone NAAQS. Any single ozone control measure is likely to produce a small reduction in ozone concentrations. It is the sum of all control measures that results in attainment of the ozone NAAQS, and the use of least-cost measures (such as HiTEC 3000) is what produces a cost-effective ozone control strategy. Based on current EPA policy, and the fact that it has been calculated that HiTEC 3000 will reduce peak ozone concentrations, then the use of HiTEC 3000 will in no way endanger attainment of the ozone NAAQS and may in fact even help a little.
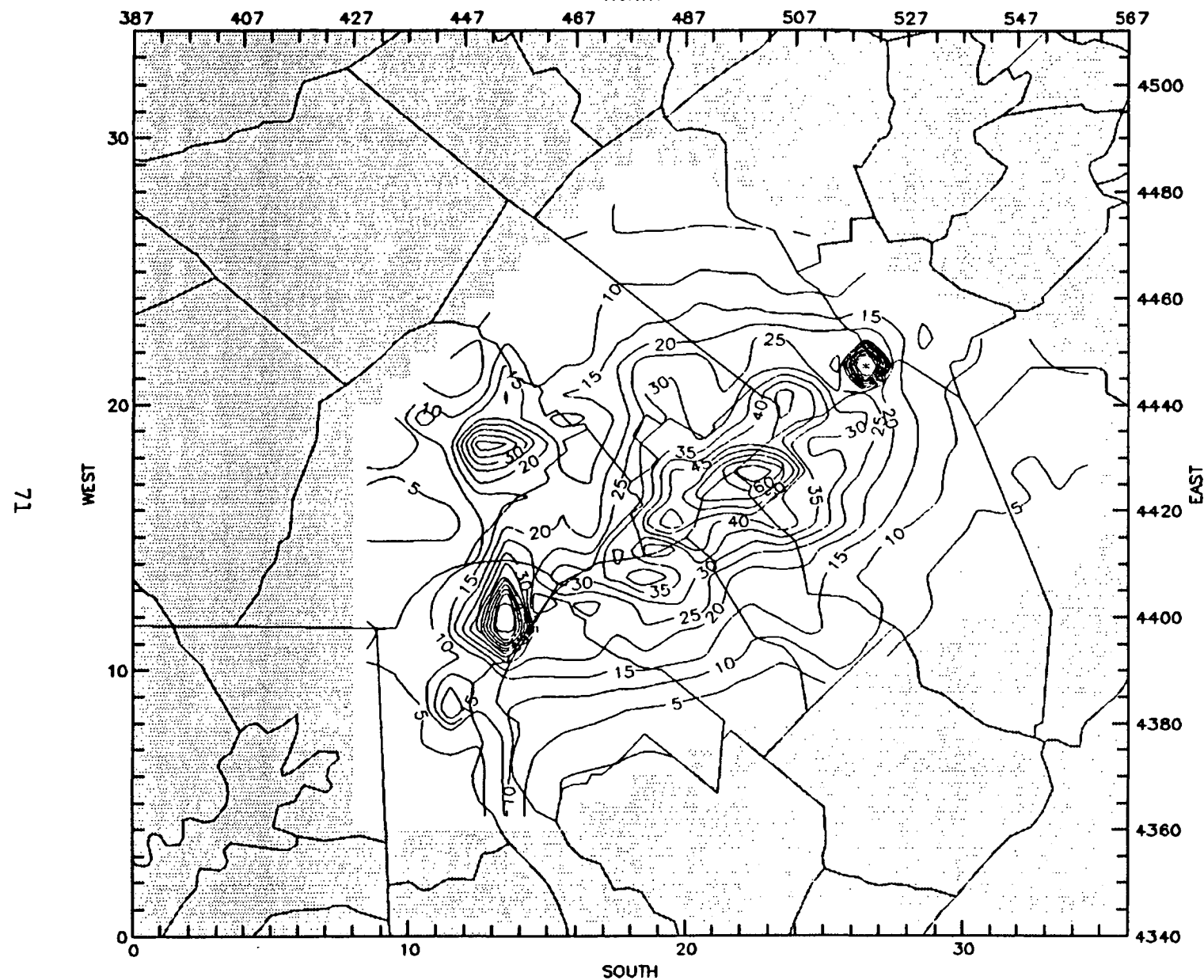
FIGURE 5-3a. Predicted daily maximum NO$_2$ concentration (ppb) in Philadelphia on July 13, 1979 for the 1994 scenario using (1) mass emissions calculated by the standard MOBILE 4 program and (2) hydrocarbon speciation based on commercial fuel plus aromatics.
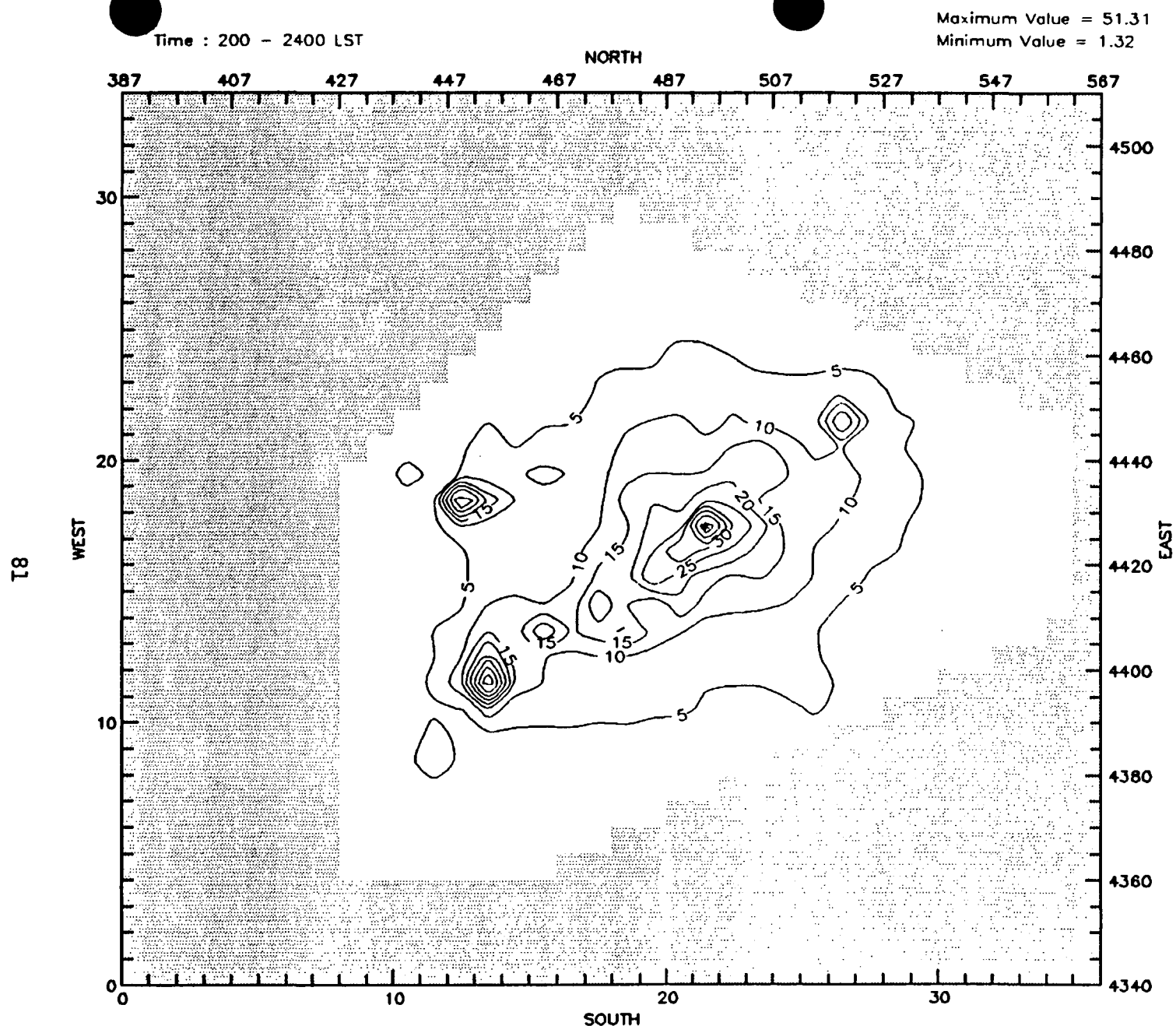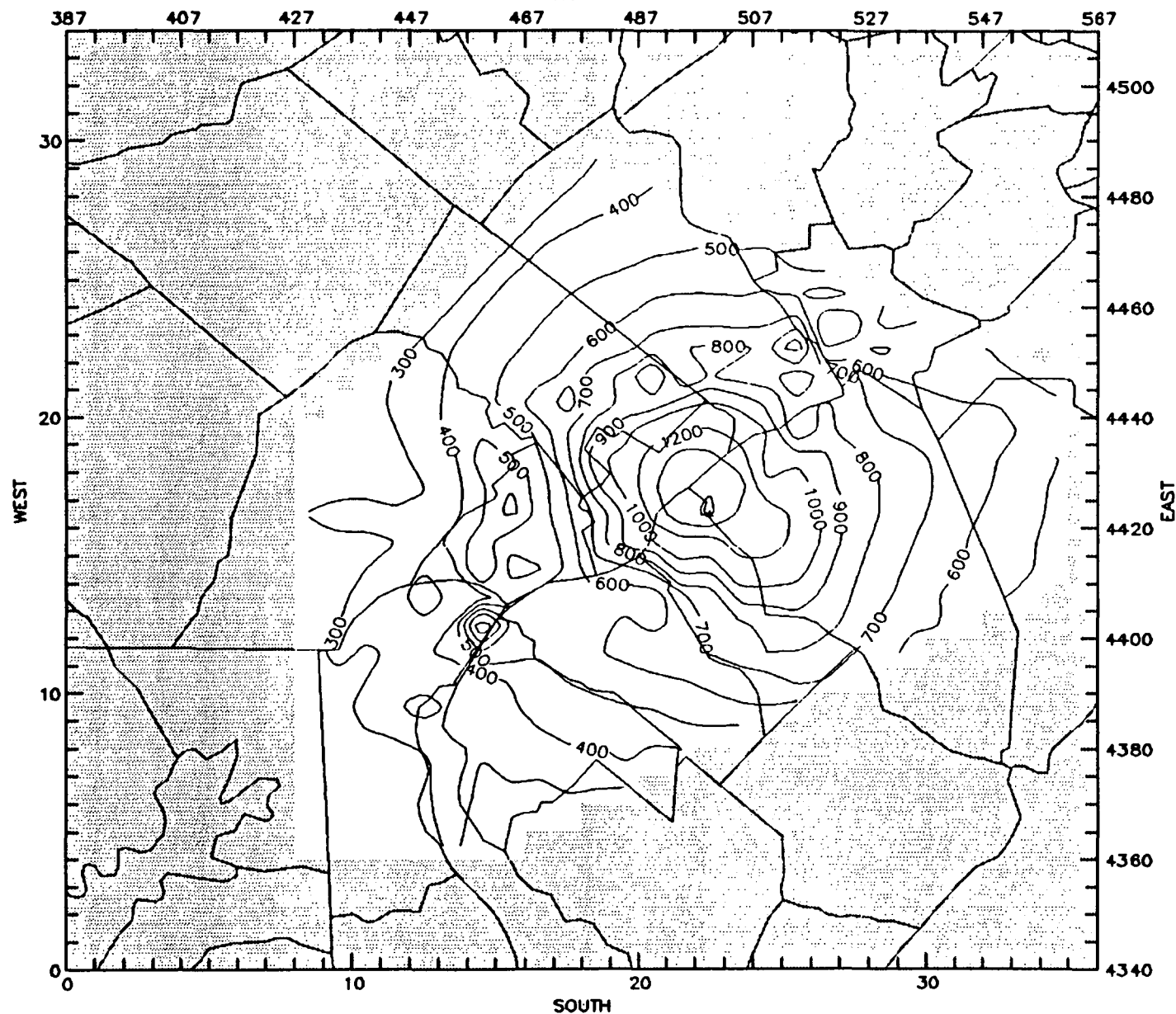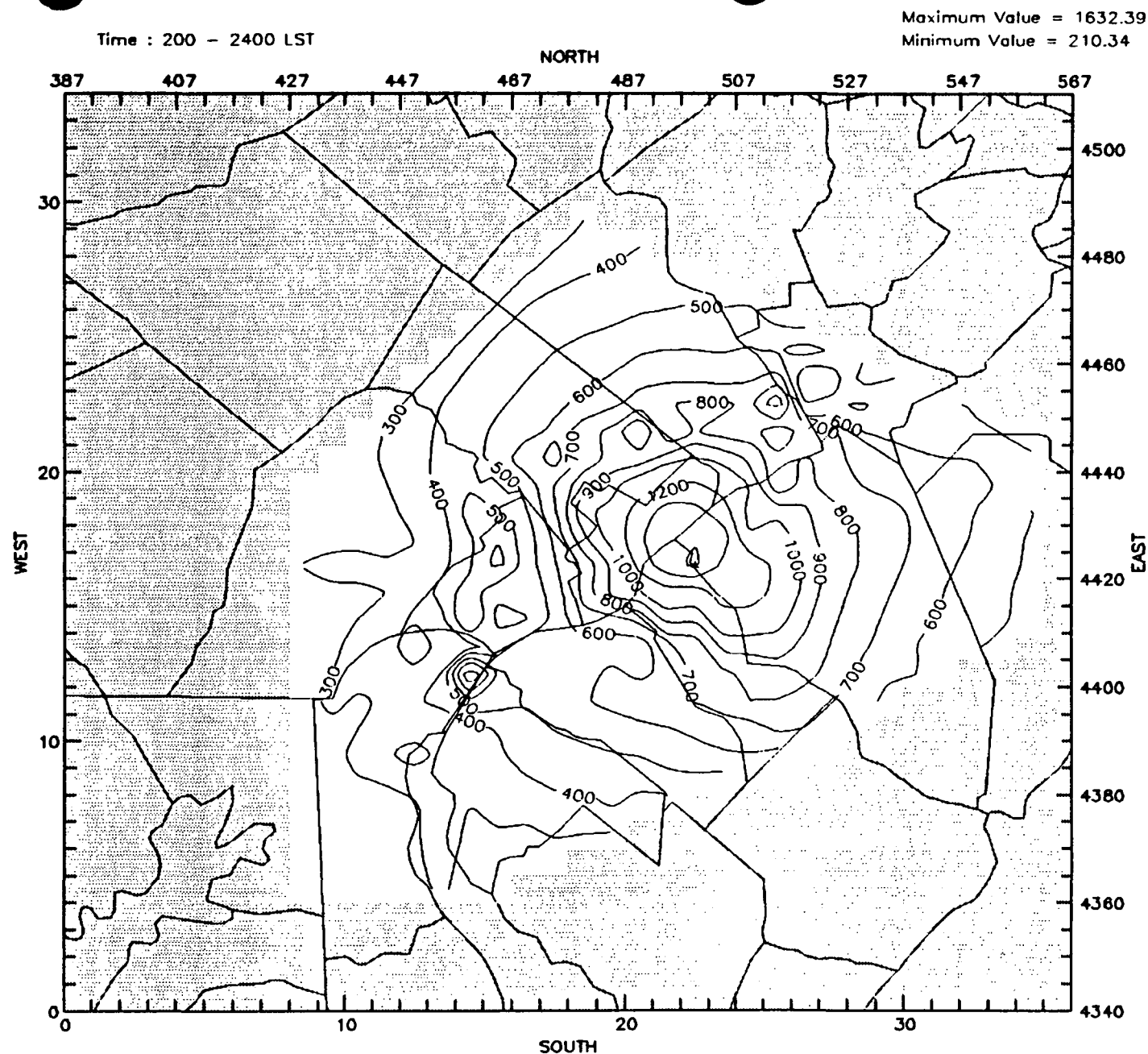
Time : 200 — 2400 LST

Maximum Value = 93.50
Minimum Value = 2.23
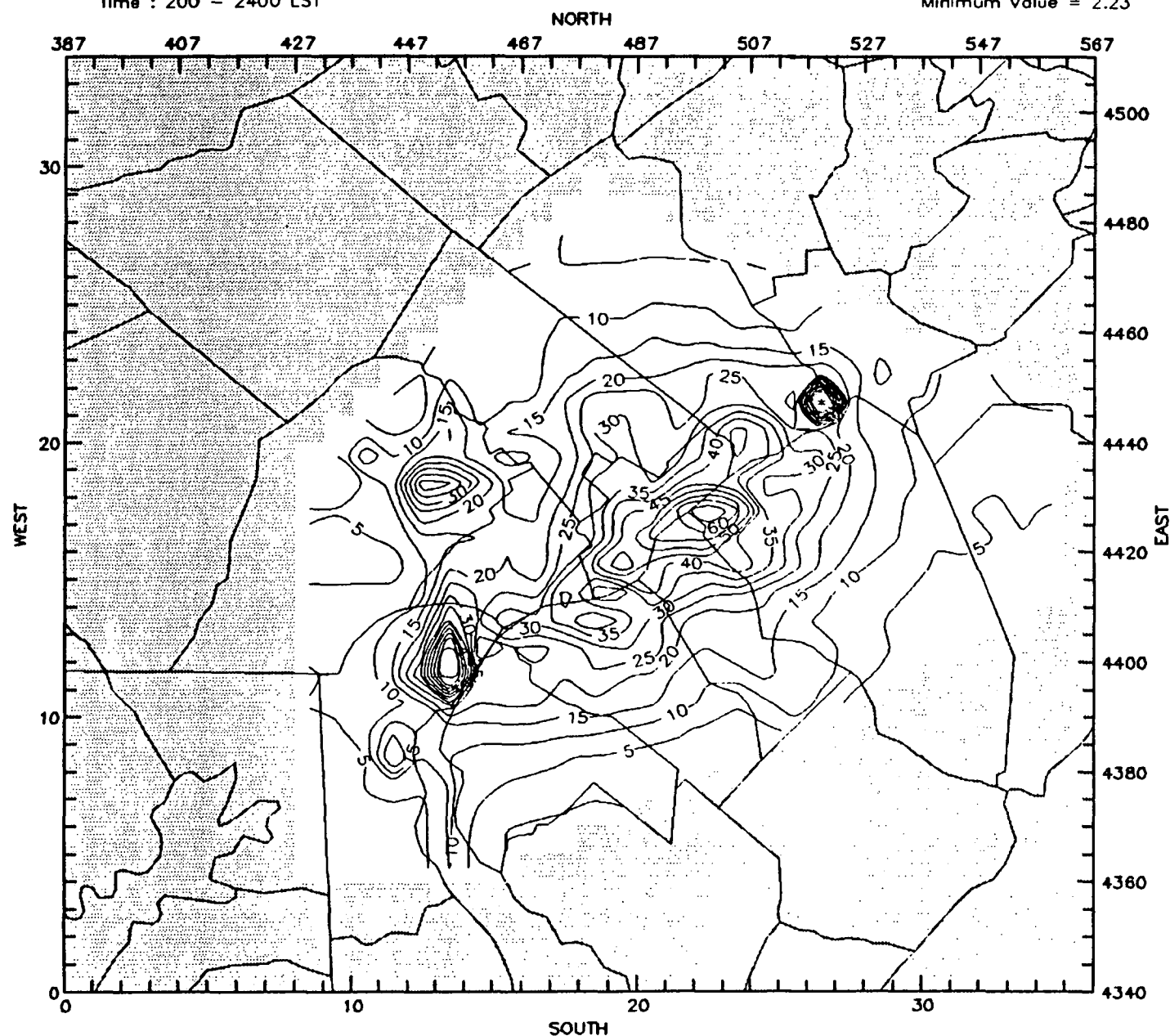
FIGURE 5-3b. Predicted daily maximum NO$_2$ concentrations (ppb) in Philadelphia on July 13, 1979 for the 1994 emissions scenario using (1) mass emissions calculated by the MOBILE 4 program modified to reflect the effects of HiTEC 3000 and (2) hydrocarbon speciation based on commercial fuel plus HiTEC 3000.
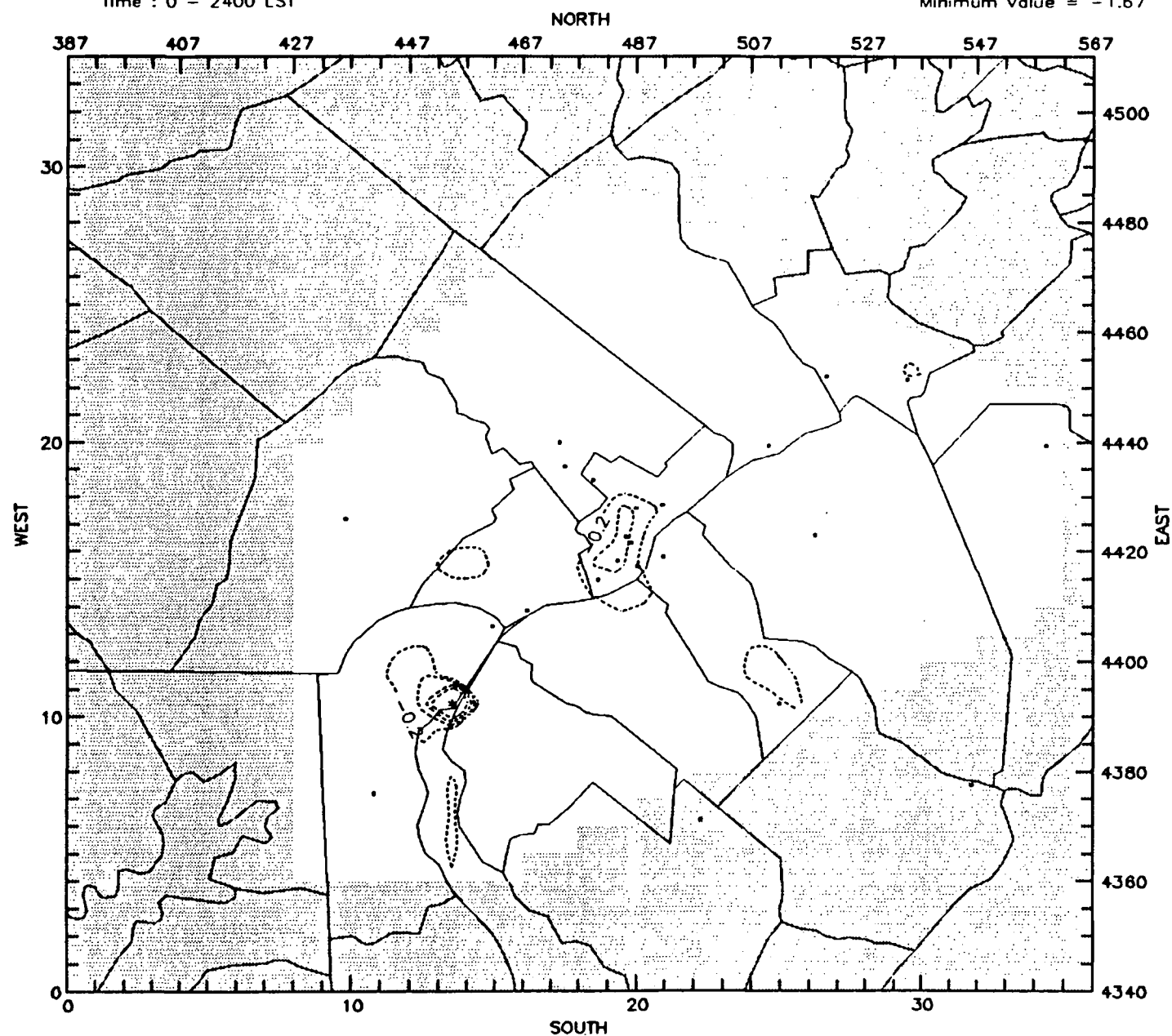
FIGURE 5-3c. Difference in daily maximum NO$_2$ concentrations (ppb) between predictions shown in Figures 5-3a and b.
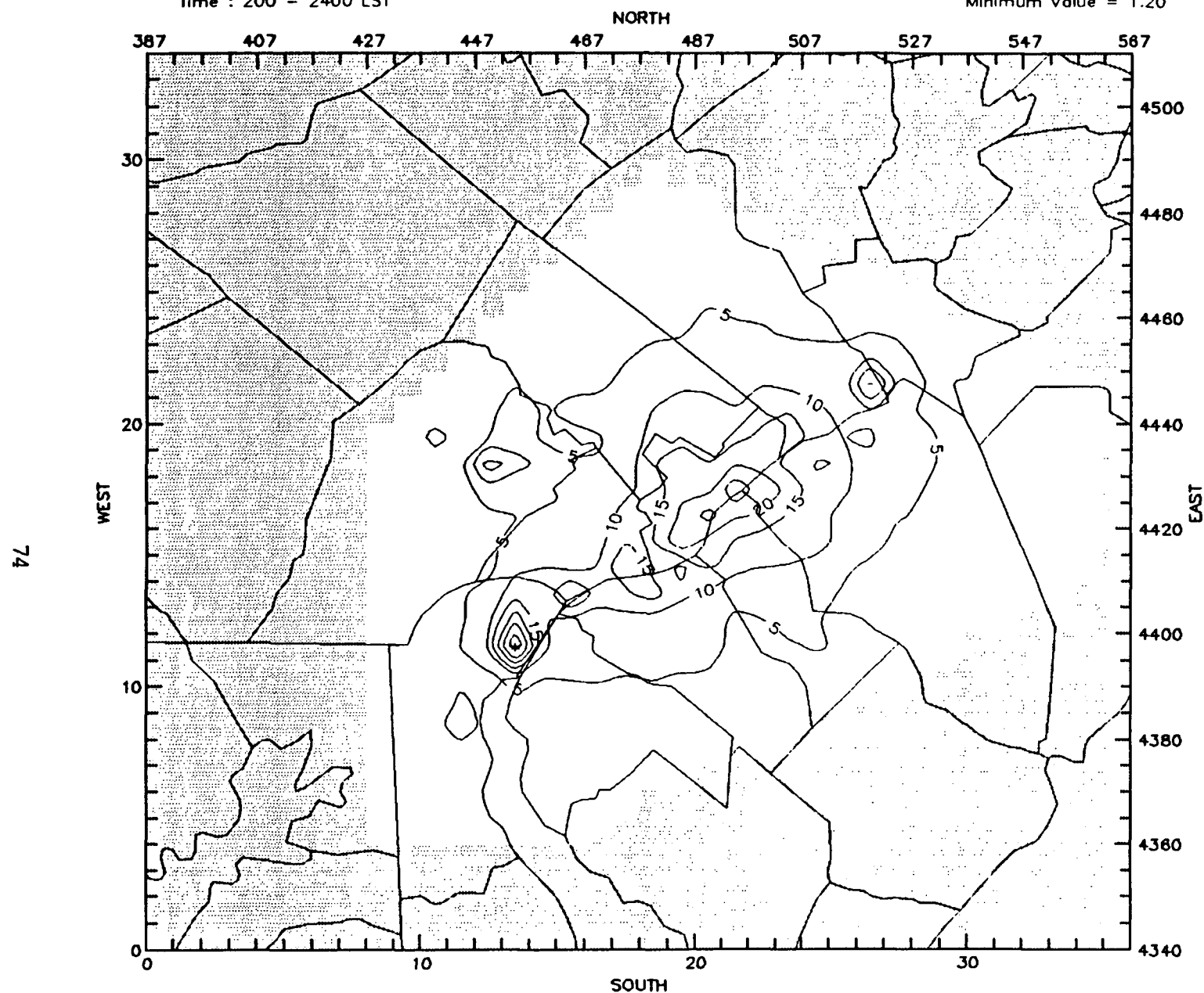
FIGURE 5-4a. Predicted 24-hour average NO$_2$ concentrations (ppb) in Philadelphia on July 13, 1979 for the 1994 emissions scenario using (1) mass emissions calculated by the standard MOBILE 4 program and (2) hydrocarbon speciation based on commercial fuel plus aromatics.
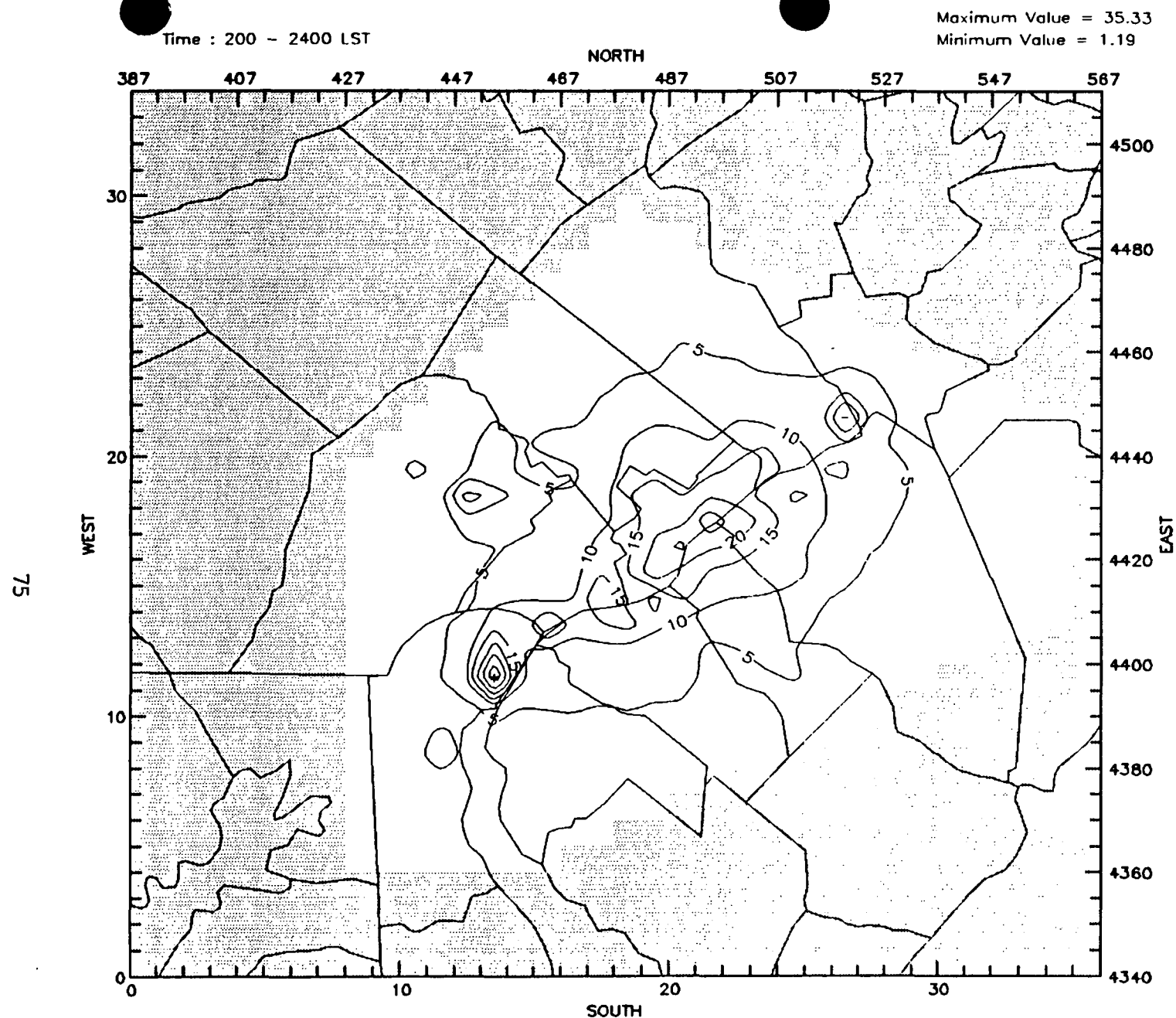
FIGURE 5-4b. Predicted 24-hour average NO$_2$ concentrations (ppb) in Philadelphia on July 13, 1979 for the 1994 emissions scenario using (1) mass emissions calculated by the MOBILE 4 program modified to reflect the effects of HiTEC 3000 and (2) hydrocarbon speciation based on commercial fuel plus HiTEC 3000.
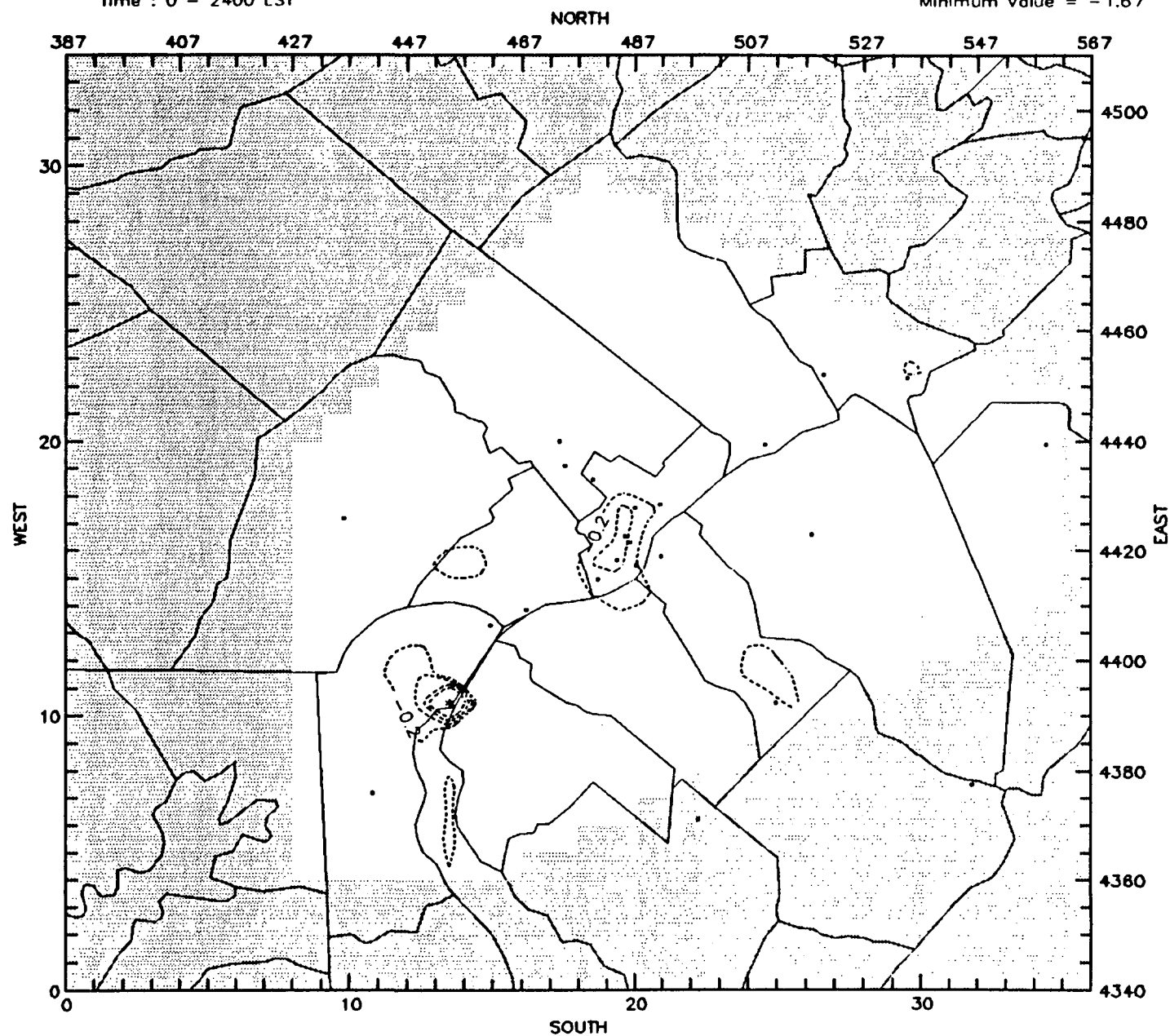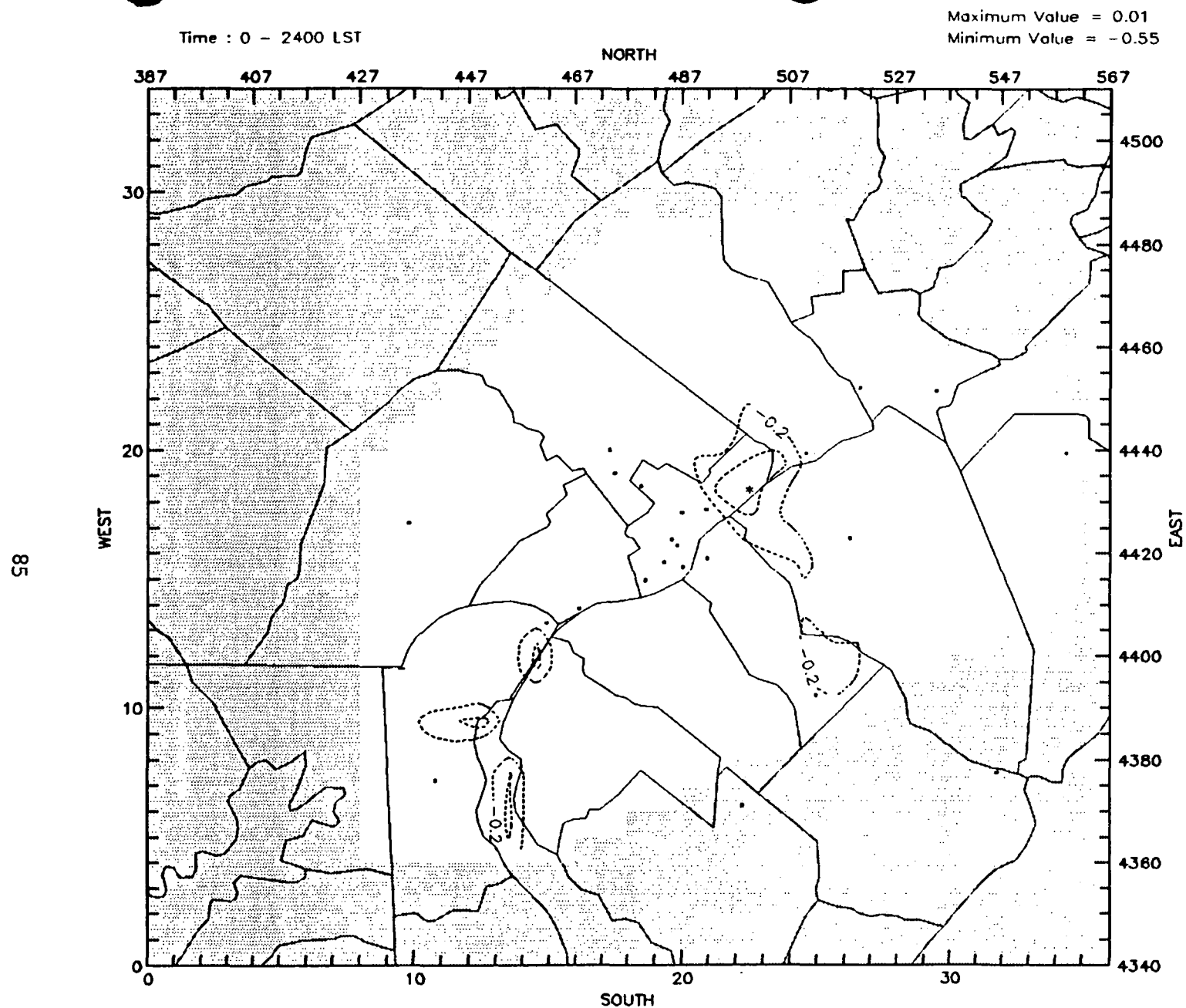
FIGURE 5-4c. Difference of 24-hour average NO_2 concentrations (ppb) between predictions shown in Figures 5-4a and b.
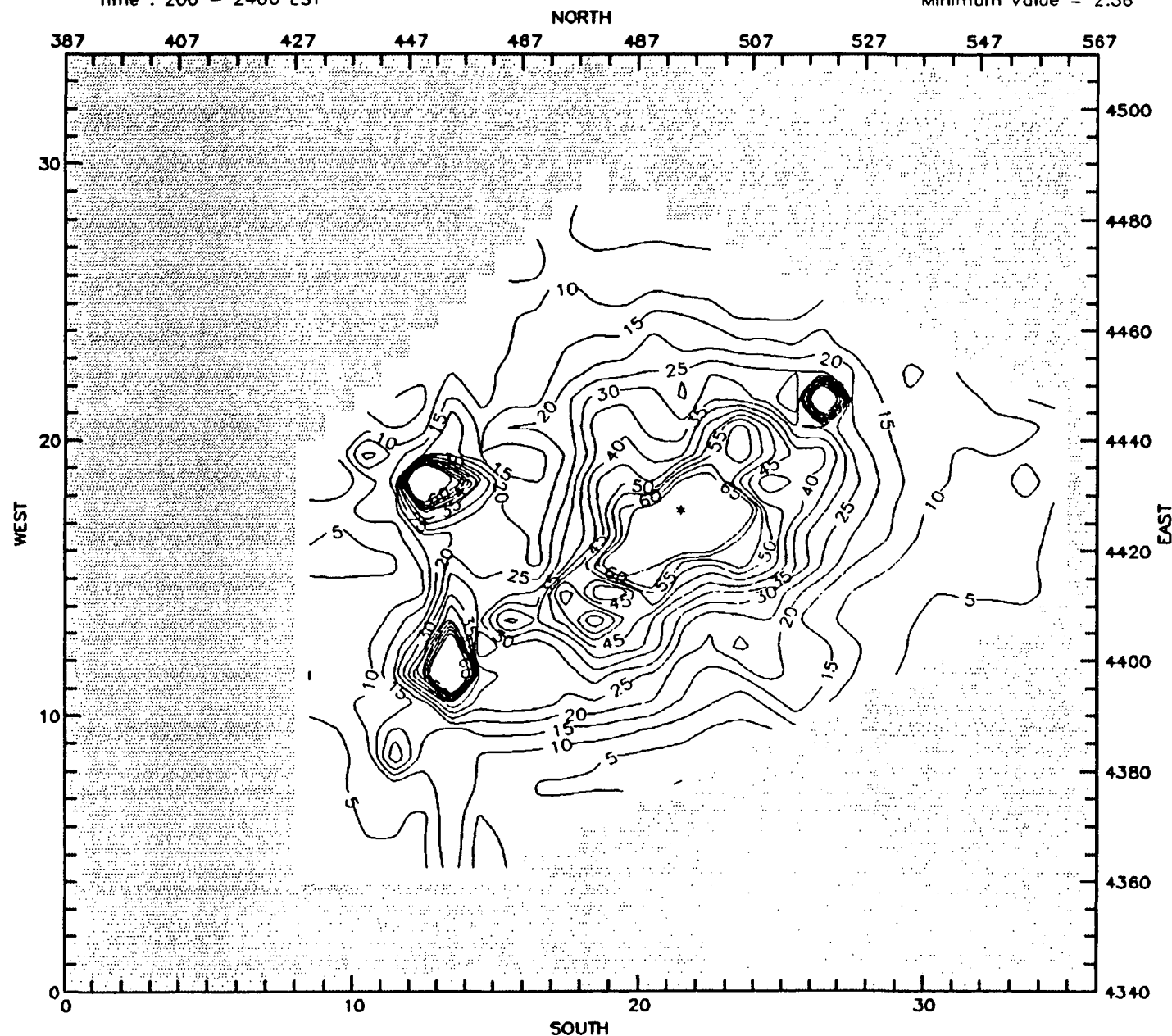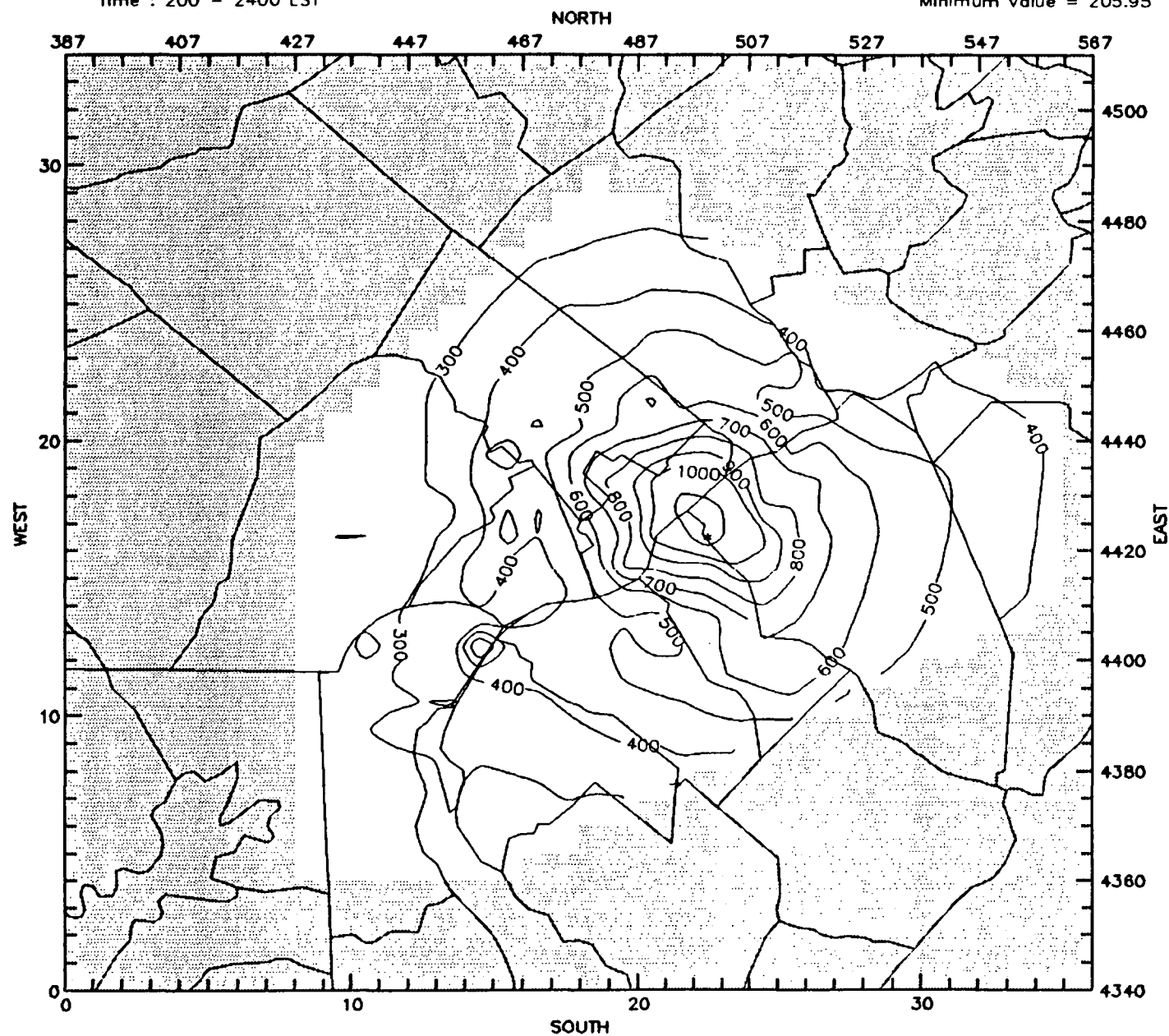
FIGURE 5-5a. Predicted daily maximum NO_x concentrations (ppb) in Philadelphia on 13 July 1979 for the 1994 emissions scenario using (1) mass emissions calculated by the standard MOBILE 4 program and (2) hydrocarbon speciation based on commercial fuel plus aromatics.
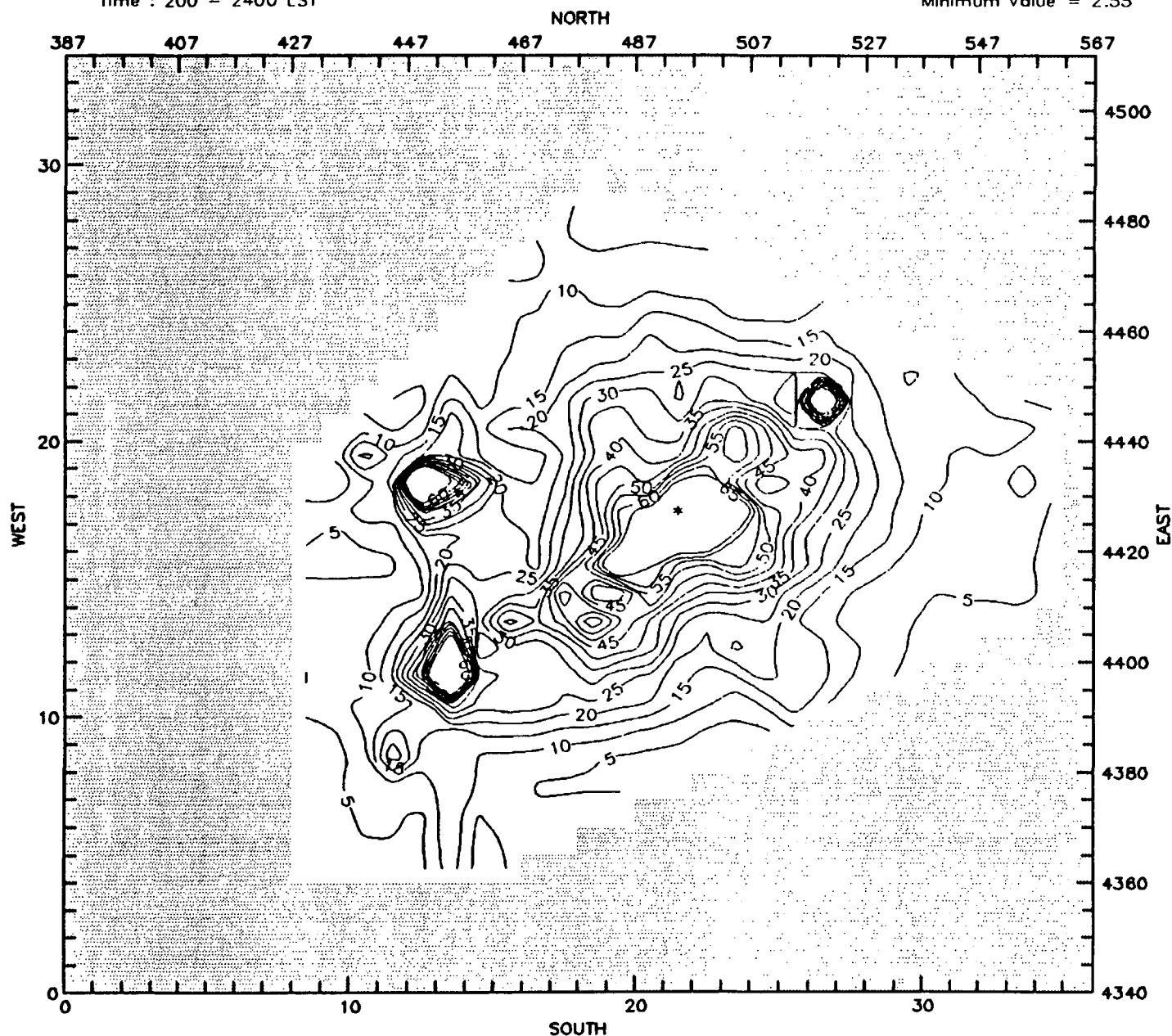
FIGURE 5-5b. Predicted daily maximum NO_x concentrations (ppb) in Philadelphia on July 13, 1979 for the 1994 emissions scenario using (1) mass emissions calculated by the MOBILE 4 program modified to reflect the effects of HiTEC 3000 and (2) hydrocarbon speciation based on commercial fuel plus HiTEC 3000.
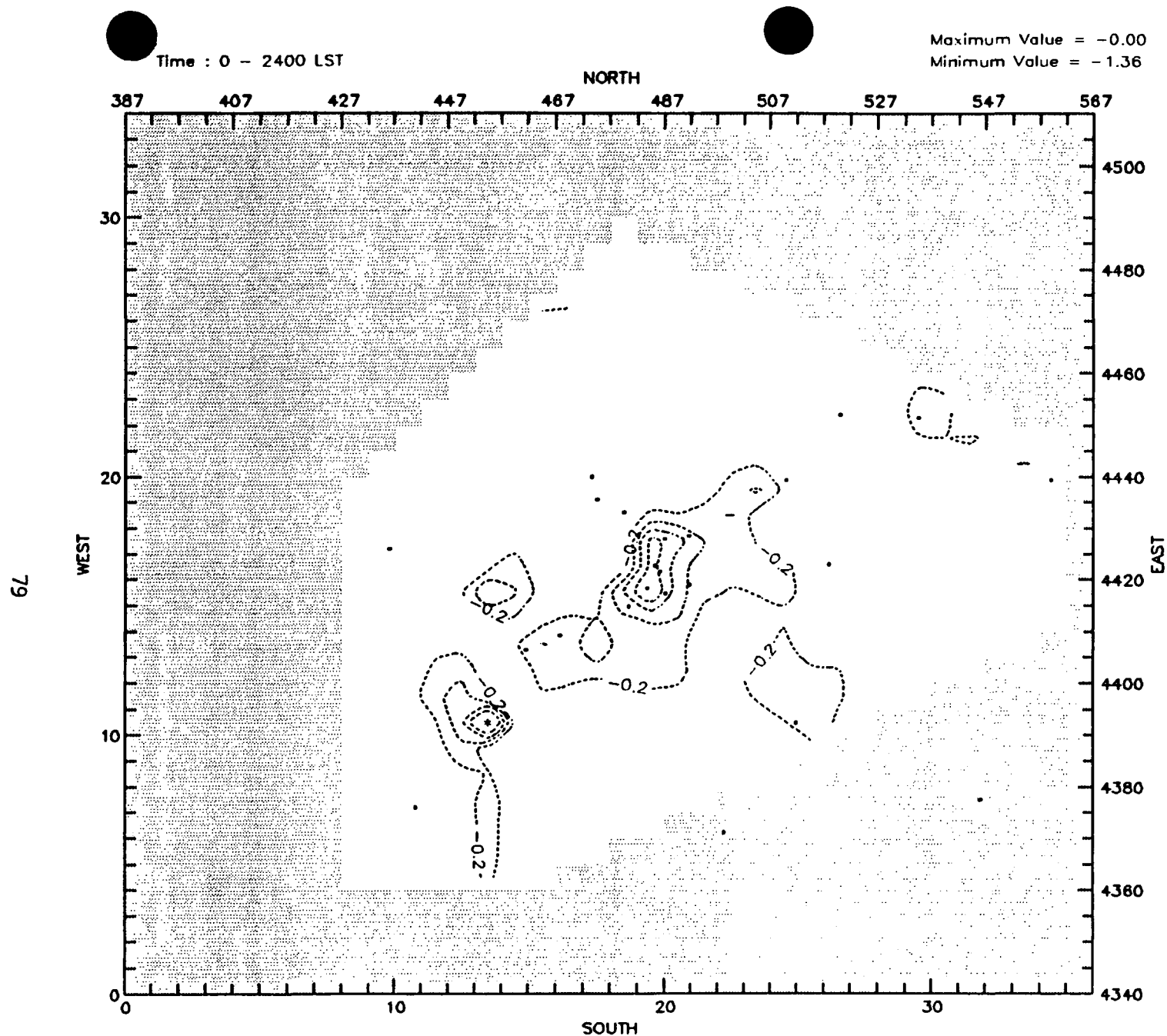
FIGURE 5-5c. Difference in daily maximum NO_x concentrations (ppb) between predictions shown in Figures 5-5a and b.
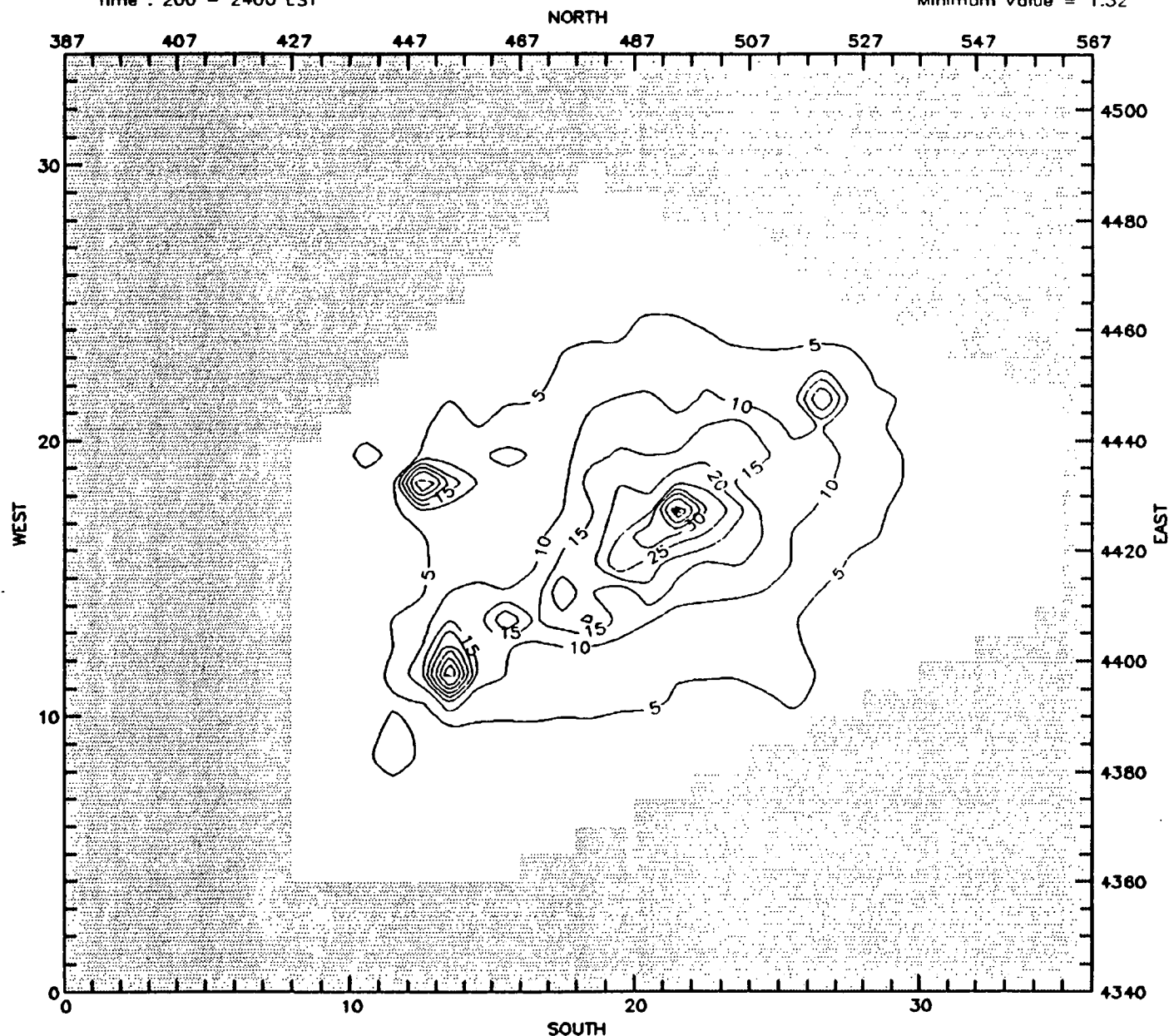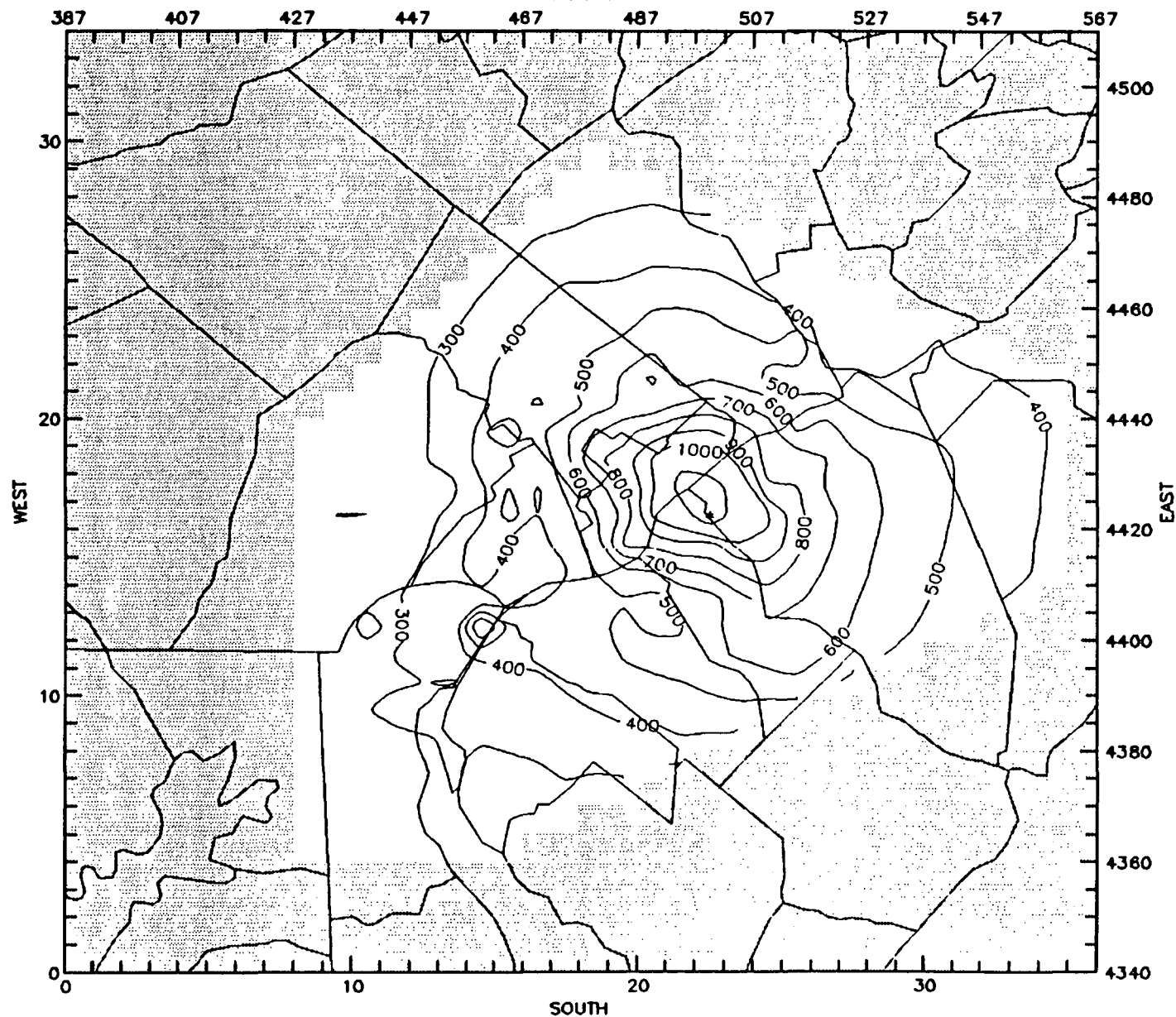
FIGURE 5-6a. Predicted 24-hour average NO_x concentrations (ppb) in Philadelphia on July 13, 1979 for the 1994 emissions scenario using (1) mass emissions calculated by the standard MOBILE 4 program and (2) hydrocarbon speciation based on commercial fuel plus aromatics.

FIGURE 5-6b. Predicted 24-hour average NO$_x$ concentrations (ppb) in Philadelphia on July 13, 1979 for the 1994 emissions scenario using (1) mass emissions calculated by the MOBILE 4 program modified to reflect the effects of HiTEC 3000 and (2) hydrocarbon speciation based on commercial fuel plus HiTEC 3000.
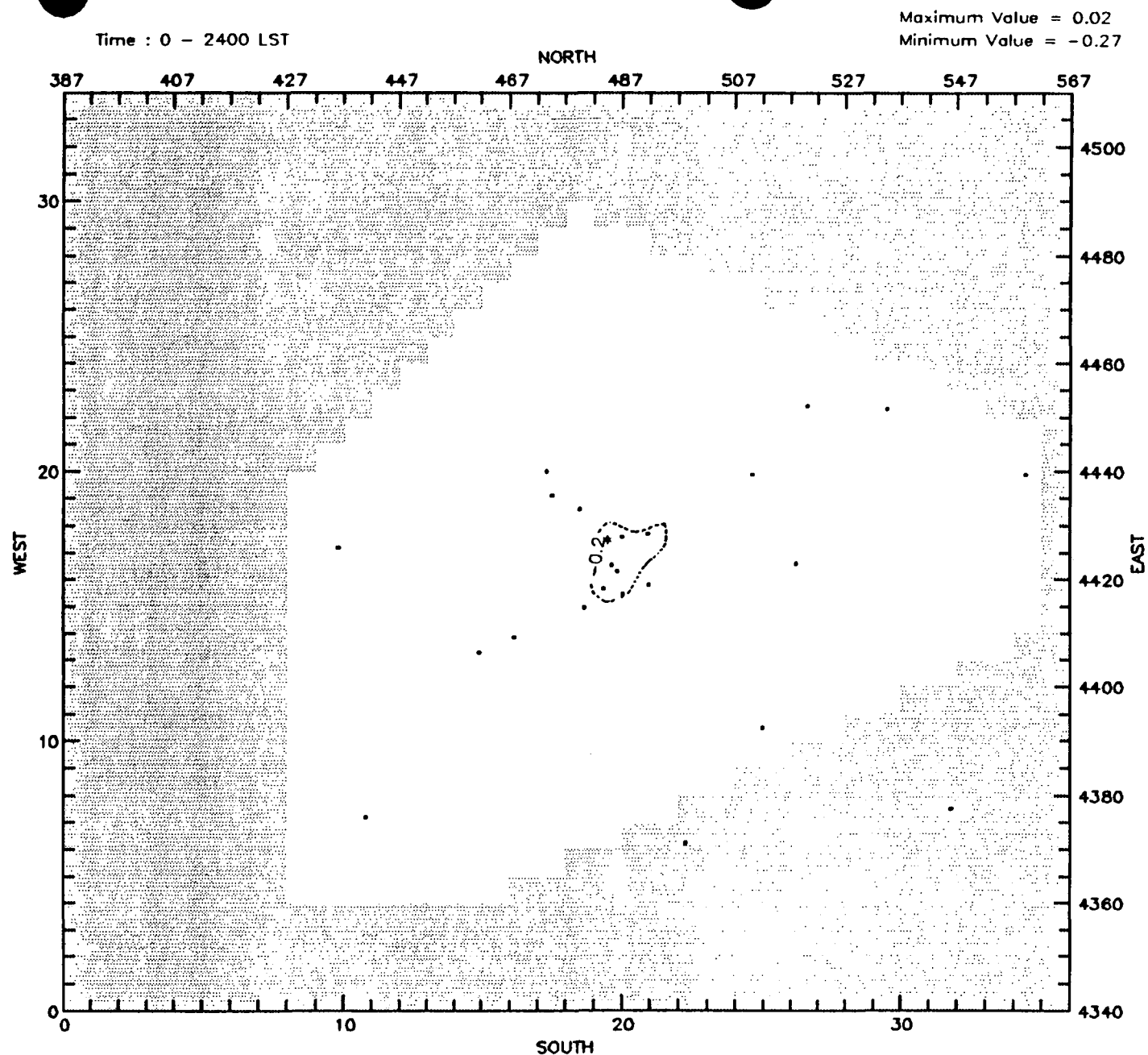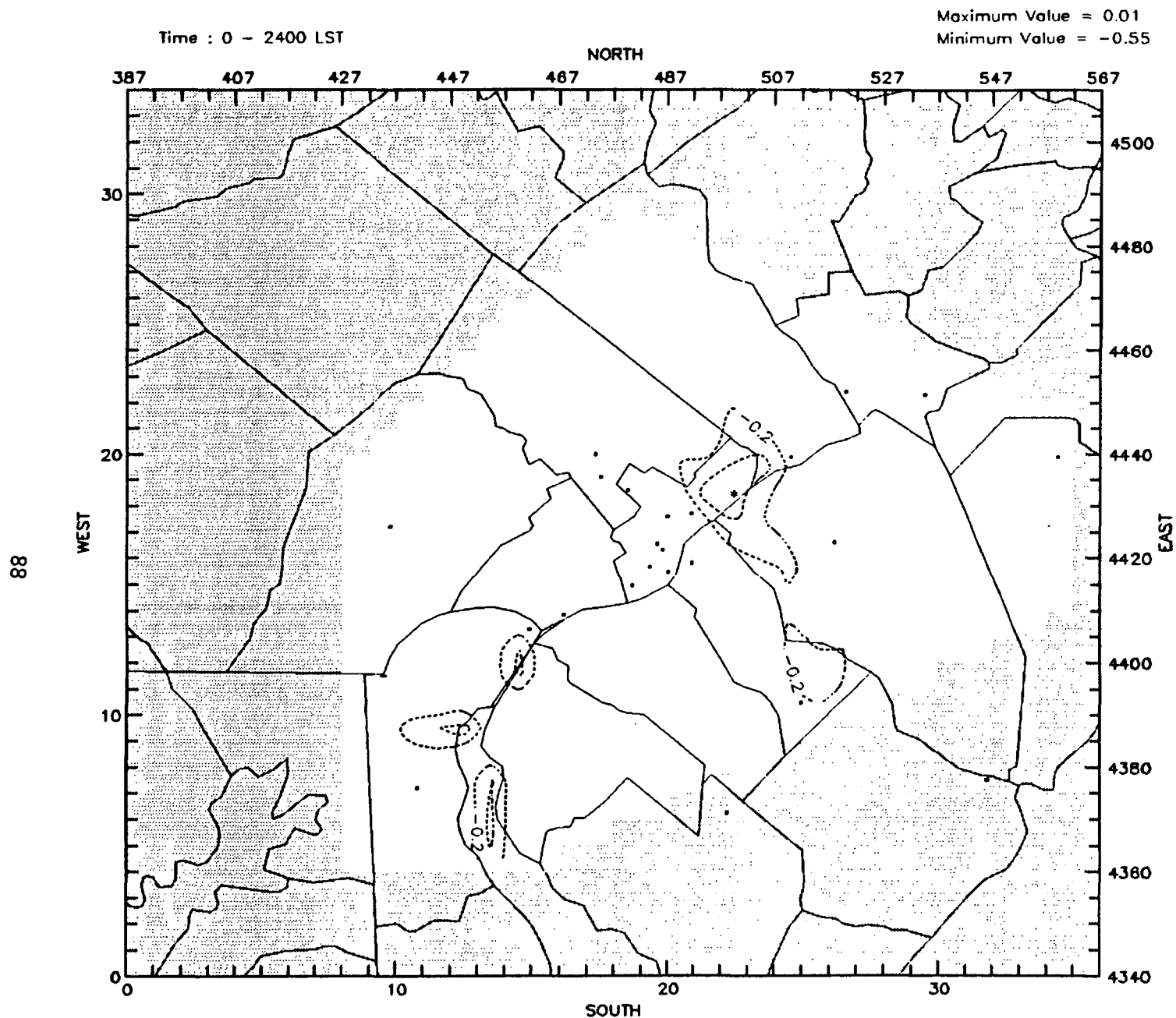
FIGURE 5-6c. Difference in 24-hour NO$_x$ concentration (ppb) between predictions shown in Figures 5-6a and b.

Time : 200 – 2400 LST

Maximum Value = 1632.61
Minimum Value ≃ 210.35

FIGURE 5-7a. Predicted daily maximum CO concentrations (ppb) in Philadelphia
on July 13, 1979 for the 1994 emissions scenario using (1) mass emissions calcu-
lated by the standard MOBILE 4 program and (2) hydrocarbon speciation based on
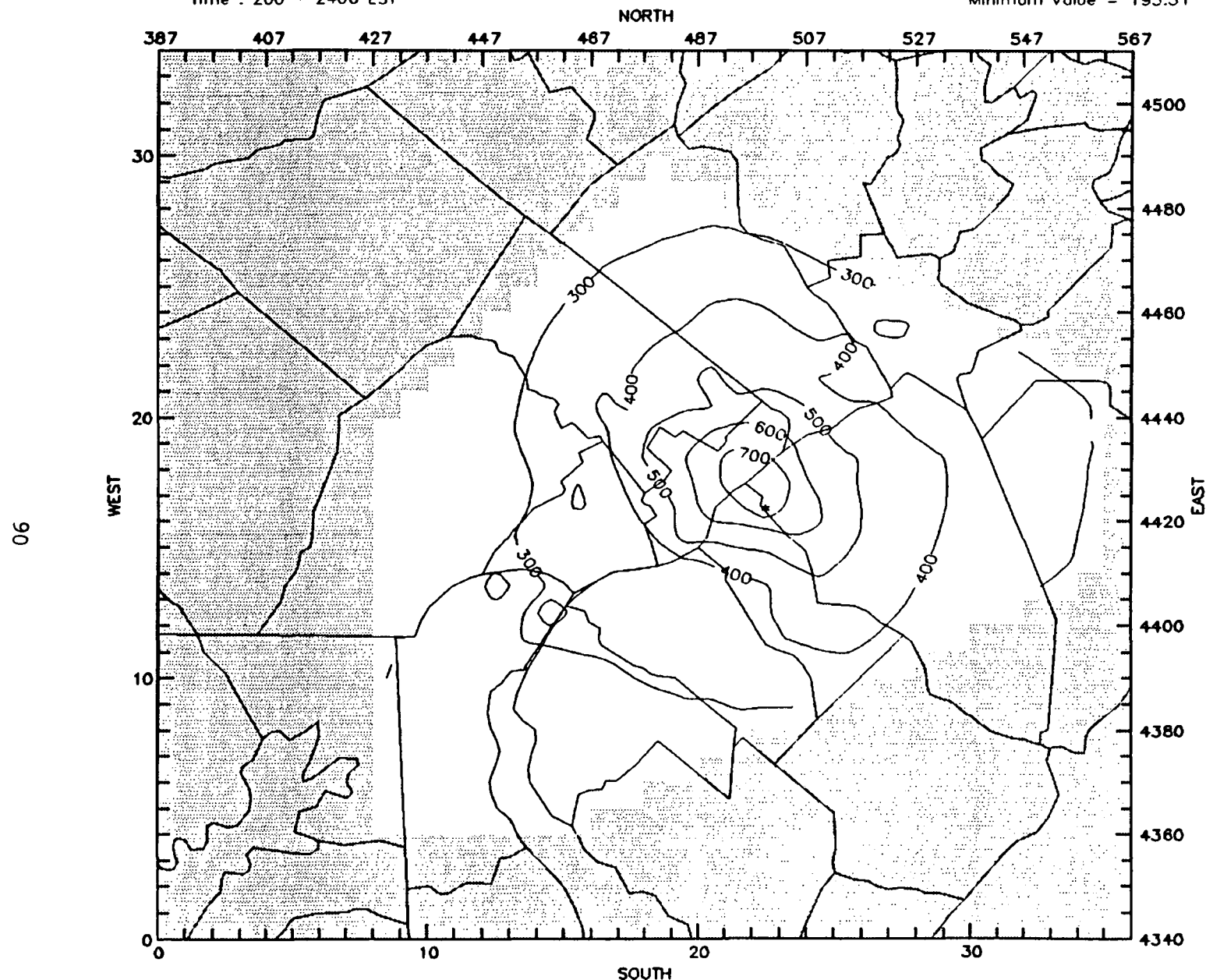commercial fuel plus aromatics.

FIGURE 5-7b. Predicted daily maximum CO concentrations (ppb) in Philadelphia on July 13, 1979 for the 1994 emissions scenario using (1) mass emissions calculated by the MOBILE 4 program modified to reflect the effects of HiTEC 3000 and (2) hydrocarbon speciation based on commercial fuel plus HiTEC 3000.

Time : 0 - 2400 LST

NORTH

Maximum Value = 0.01
Minimum Value = -0.55

FIGURE 5-7c. Difference in daily maximum CO concentration (ppb) between predictions shown in Figures 5-7a and b.

Time : 200 – 2400 LST

NORTH

FIGURE 5-8a. Predicted 8-hour average CO concentration (ppb) in Philadelphia on 13 July, 1979 for the 1994 emissions scenario using (1) mass emissions calculated by the standard MOBILE 4 program and (2) hydrocarbon speciation based on commercial fuel plus aromatics.

FIGURE 5-8b. Predicted 8-hour average CO concentrations (ppb) in Philadelphia on 13 July 1979 for the 1994 emissions scenario using (1) mass emissions calculated by the MOBILE 4 program modified to reflect the effects of HiTEC 3000 and (2) hydrocarbon speciation based on commercial fuel plus HiTEC 3000.

FIGURE 5-9c. Difference in 8-hour average CO concentration (ppb) between predictions shown in Figures 5-8a and b.
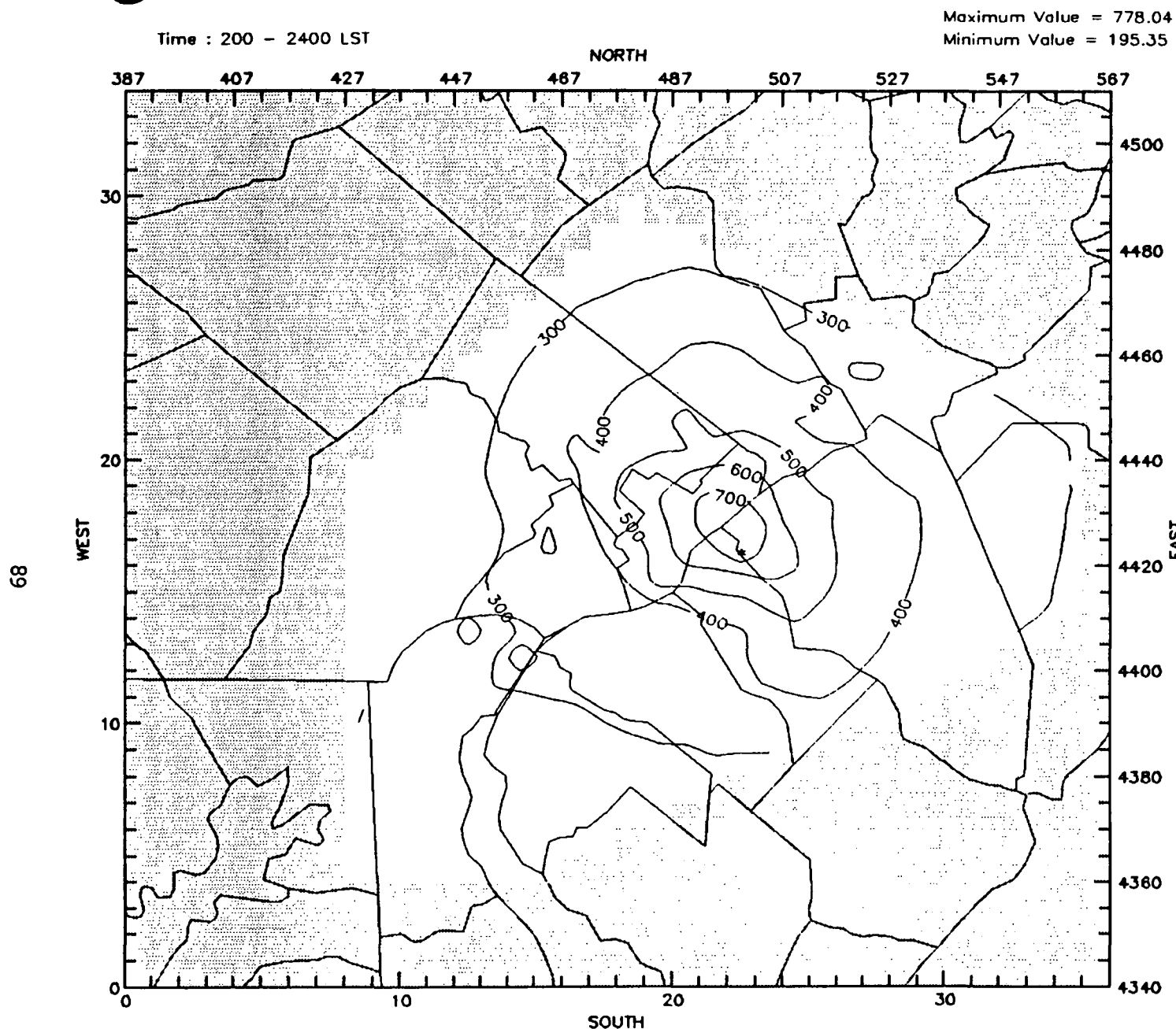
FIGURE 5-9a. Predicted 24-hour average CO concentrations (ppb) in Philadelphia on July 13, 1979 for the 1994 emissions scenario using (1) mass emissions calculated by the standard MOBILE 4 program and (2) hydrocarbon speciation based on commercial fuel plus aromatics.

Time : 200 – 2400 LST

Maximum Value = 777.82
Minimum Value = 195.31

FIGURE 5-9b. Predicted 24-hour average CO concentrations (ppb) in Philadelphia
on July 13, 1979 for the 1994 emissions scenario using (1) mass emissions calcu-
lated by the MOBILE 4 program modified to reflect the effects of HiTEC 3000 and
(2) hydrocarbon speciation based on commercial fuel plus HiTEC 3000.

Time : 0 - 2400 LST

Maximum Value = 0.01
Minimum Value = -0.55
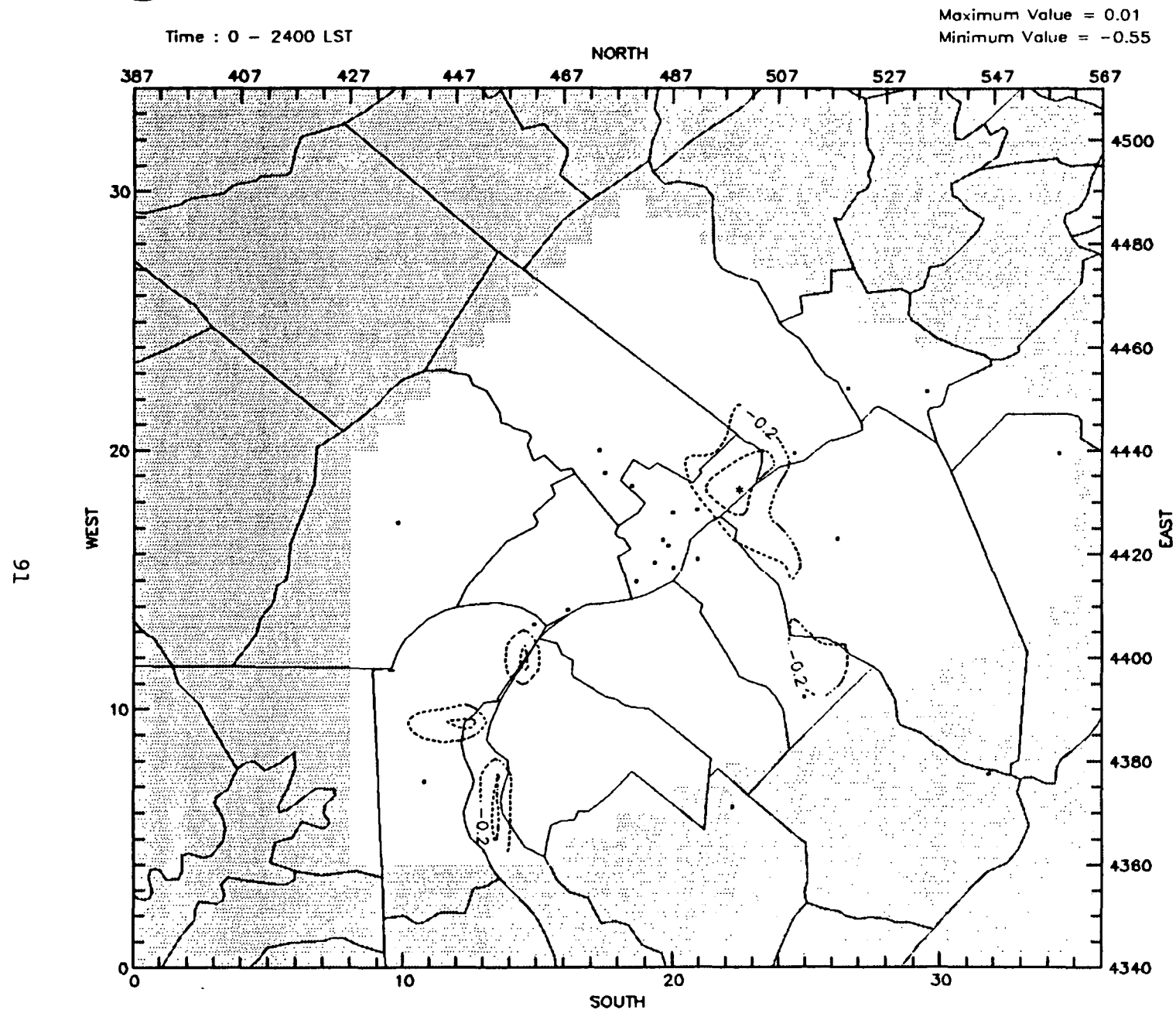
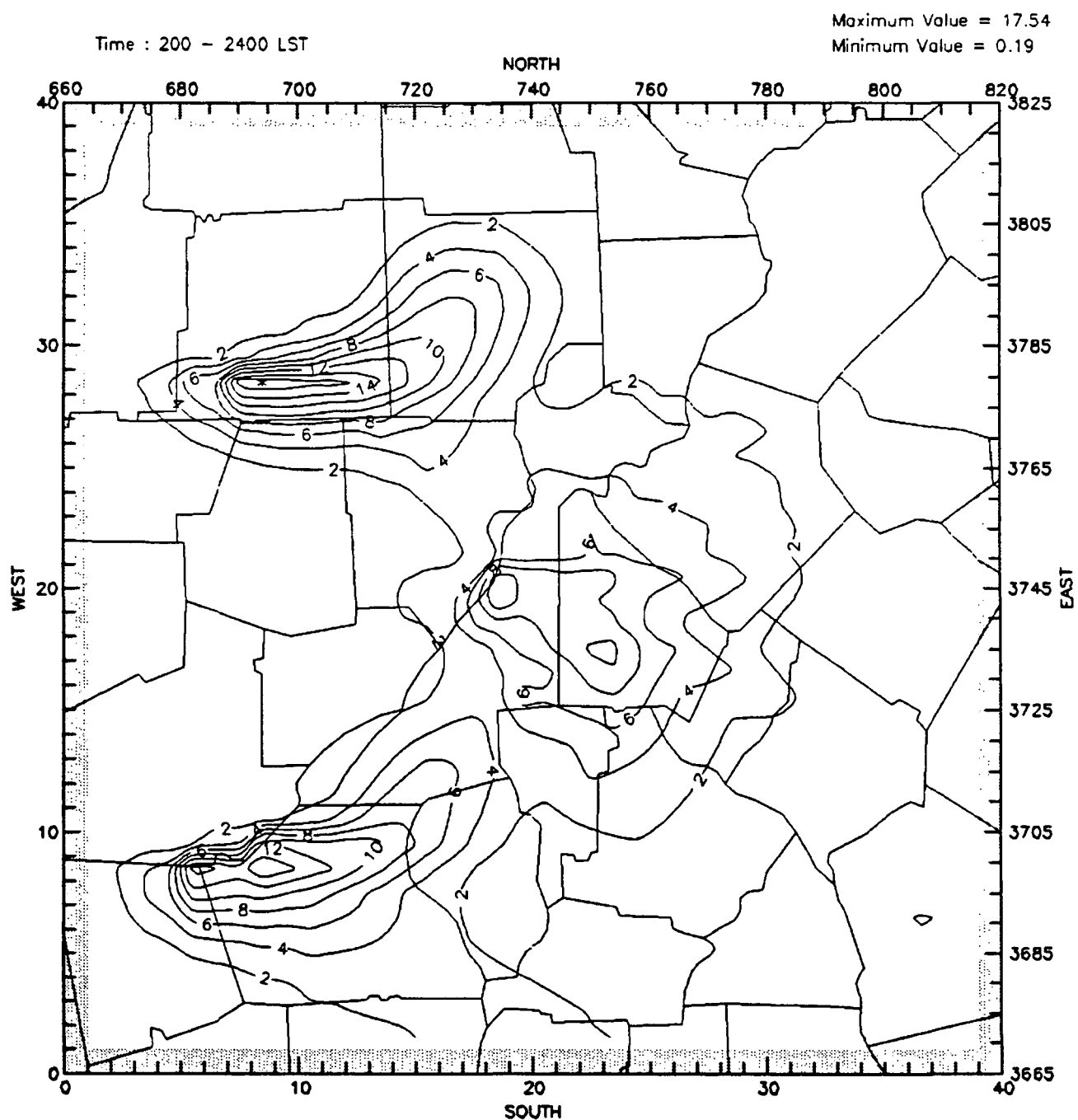FIGURE 5-9c. Difference in 24-hour average CO concentration (ppb) between predictions shown in Figures 5-9c.
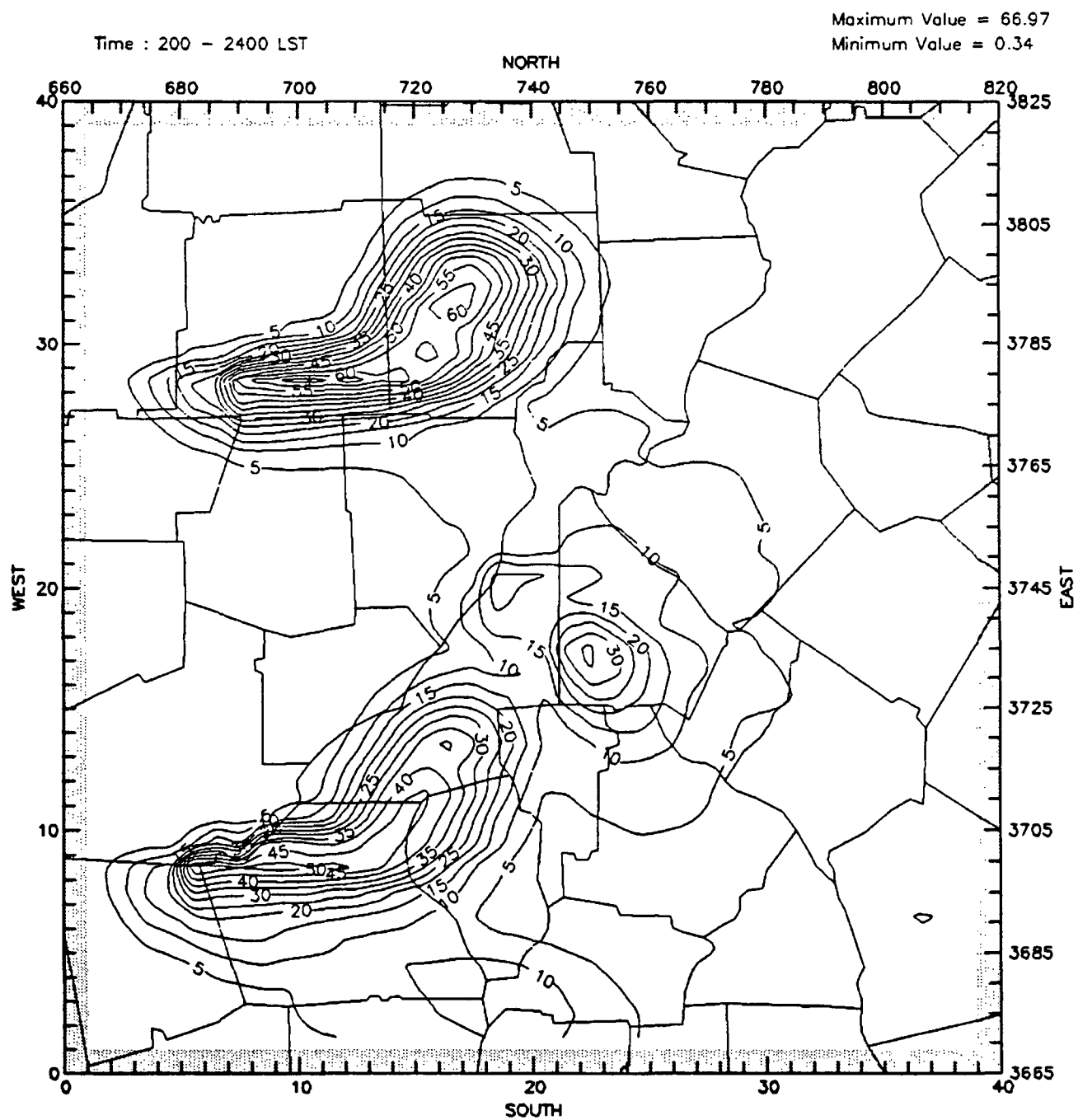
FIGURE 5-10a. Predicted daily maximum NO_2 concentration (ppb) in Atlanta on 4 June 1984 for the 1994 emissions scenario using (1) mass emissions calculated by the standard MOBILE 4 program and (2) hydrocarbon speciation based on commercial fuel plus aromatics.
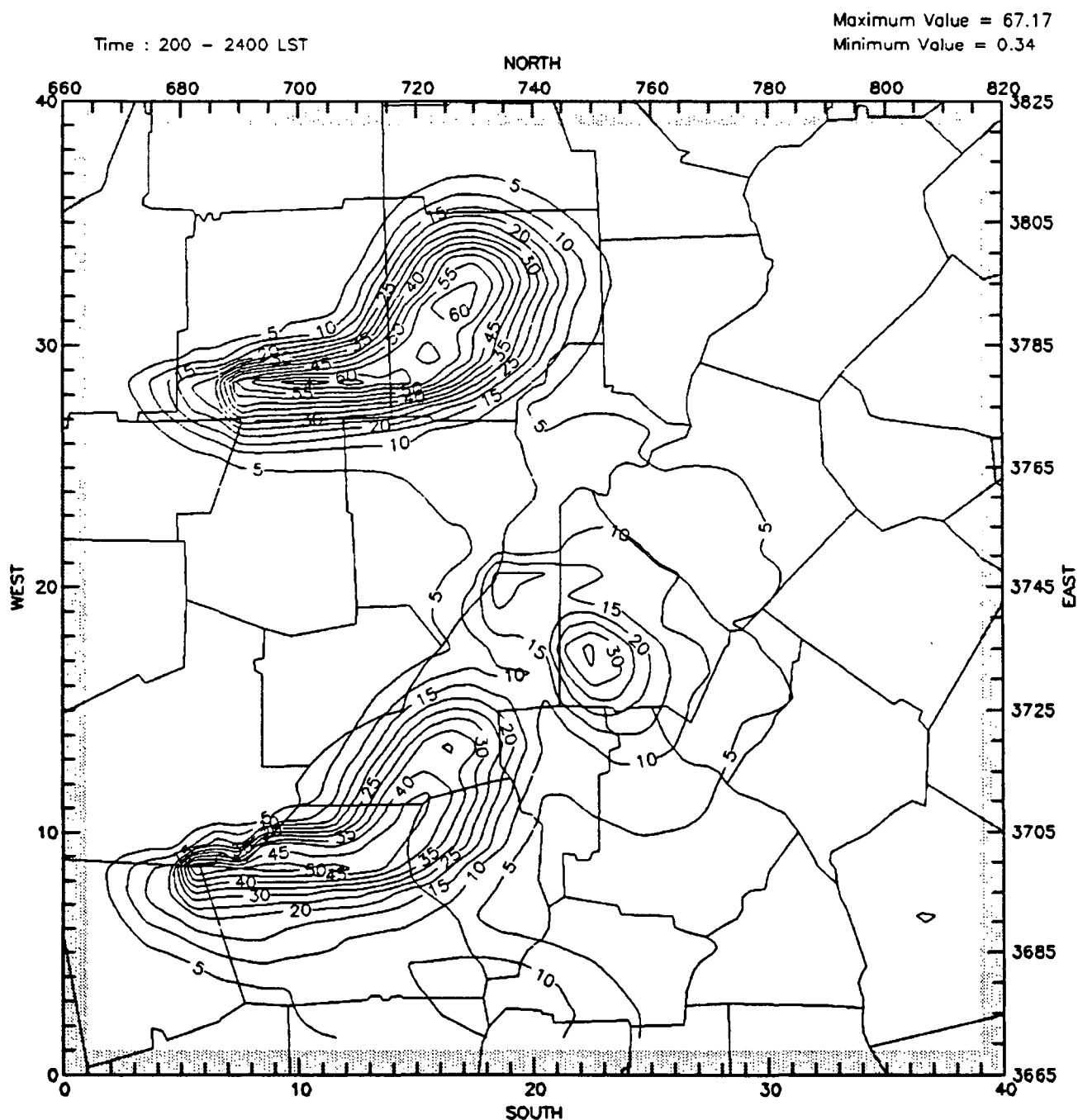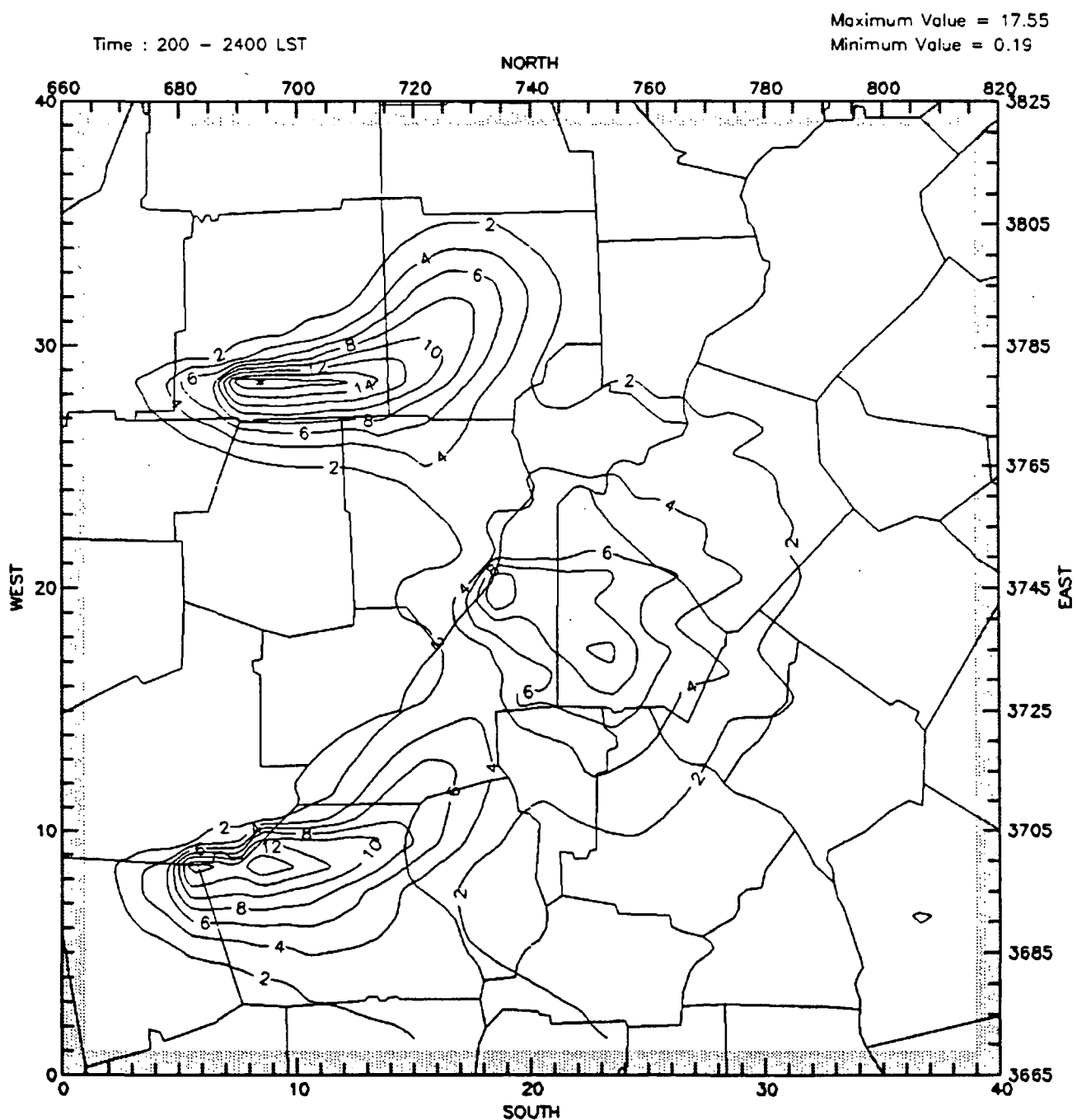
FIGURE 5-10b. Predicted daily maximum NO$_2$ concentration (ppb) in Atlanta on June 4, 1984 for the 1994 emissions scenario using (1) mass emissions calculated by the MOBILE 4 program modified to reflect the effects of HiTEC 3000 and (2) hydrocarbon speciation based on commercial fuel plus HiTEC 3000.
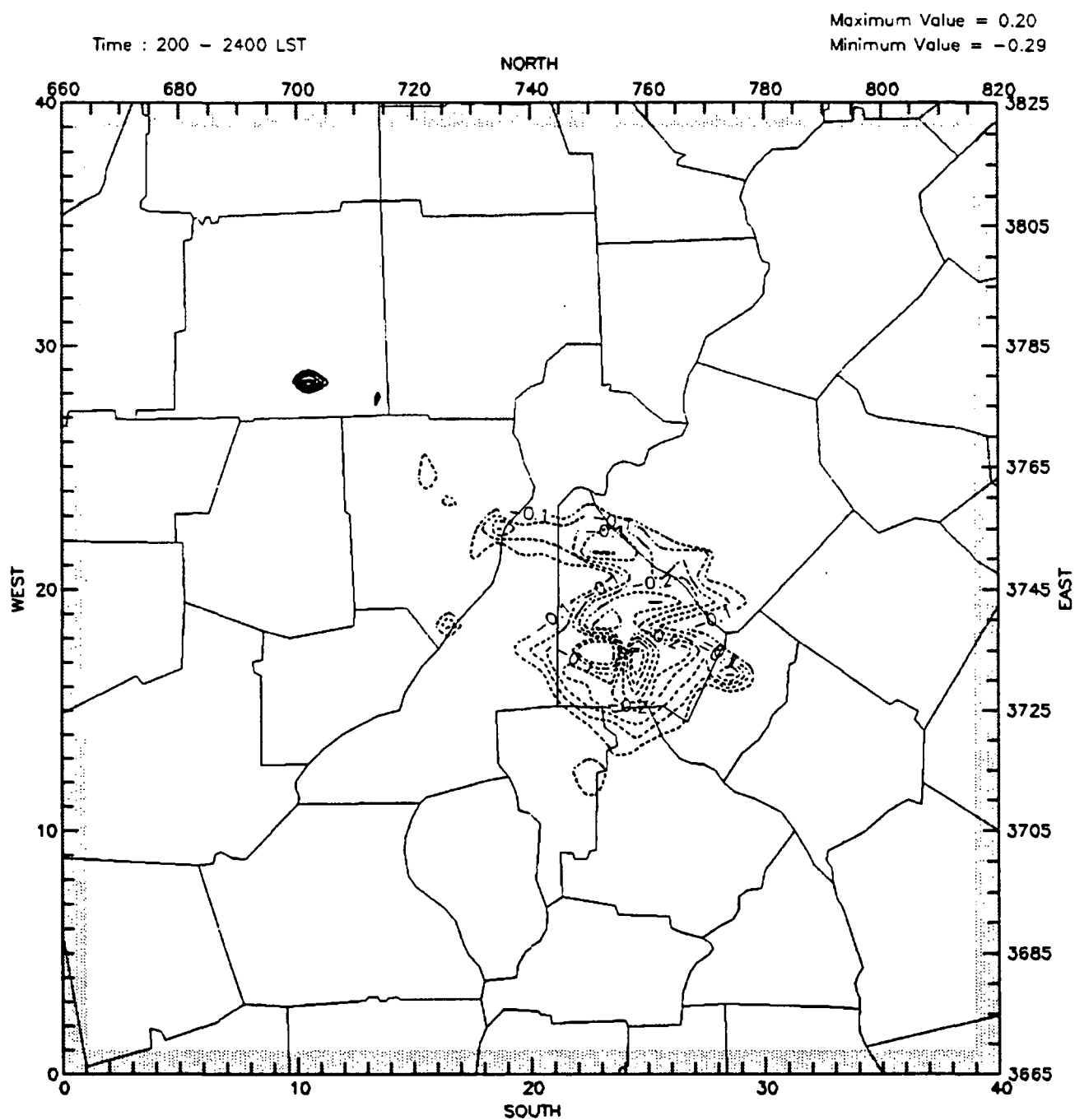
FIGURE 5-10c. Difference in daily maximum NO_2 concentration (ppb) between predictions shown in Figures 5-10a and b.

FIGURE 5-11a. Predicted 24-hour average NO$_2$ concentrations (ppb) in Atlanta on June 4, 1984 for the 1994 emissions scenario using (1) mass emissions calculated by the standard MOBILE 4 program and (2) hydrocarbon speciation based on commercial fuel plus aromatics.

FIGURE 5-11b. Predicted 24-hour average NO$_2$ concentration (ppb) in Atlanta on June 4, 1984 for the 1994 emissions scenario using (1) mass emissions calculated by the MOBILE 4 program modified to reflect the effects of HiTEC 3000 and (2) hydrocarbon speciation on commercial fuel plus HiTEC 3000.
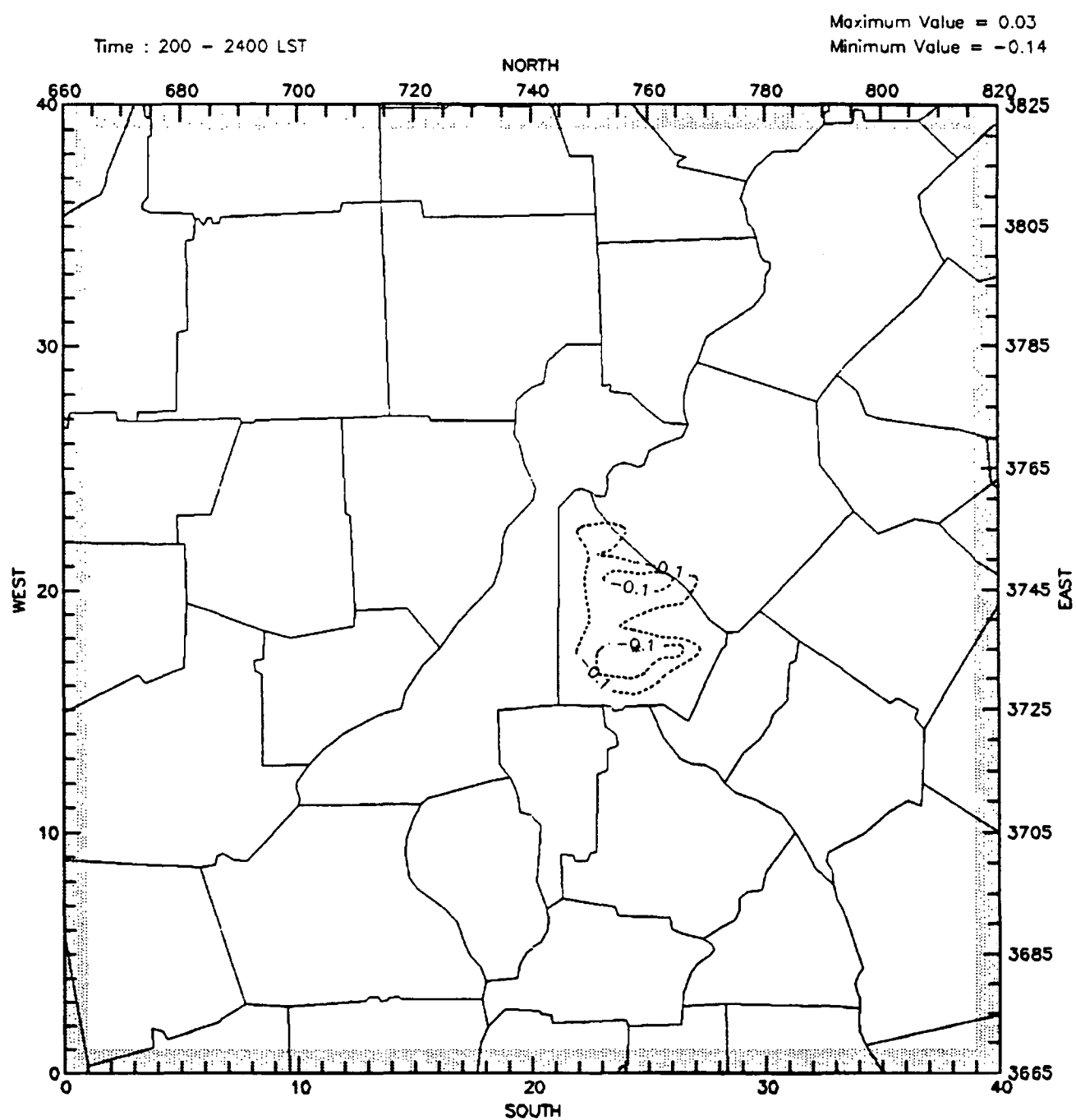
FIGURE 5-11c. Difference in 24-hour average NO$_2$ concentration (ppb) between predictions shown in Figures 5-11a and b.
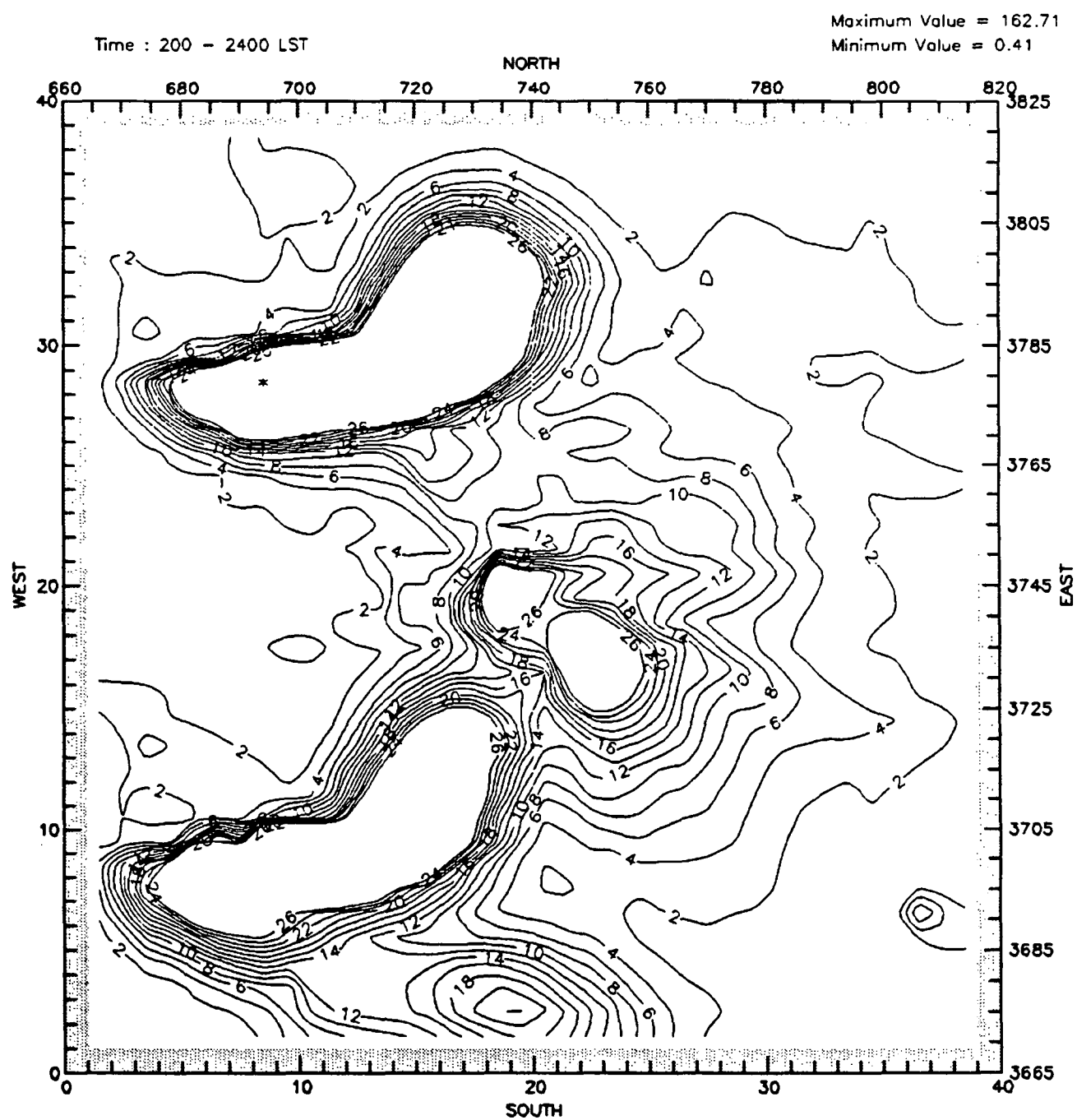
FIGURE 5-12a. Predicted daily maximum NO$_x$ concentrations (ppb) in Atlanta on June 4, 1984 for the 1994 emissions scenario using (1) mass emissions calculated by the standard MOBILE 4 program and (2) hydrocarbon speciation based on commercial fuel plus aromatics.
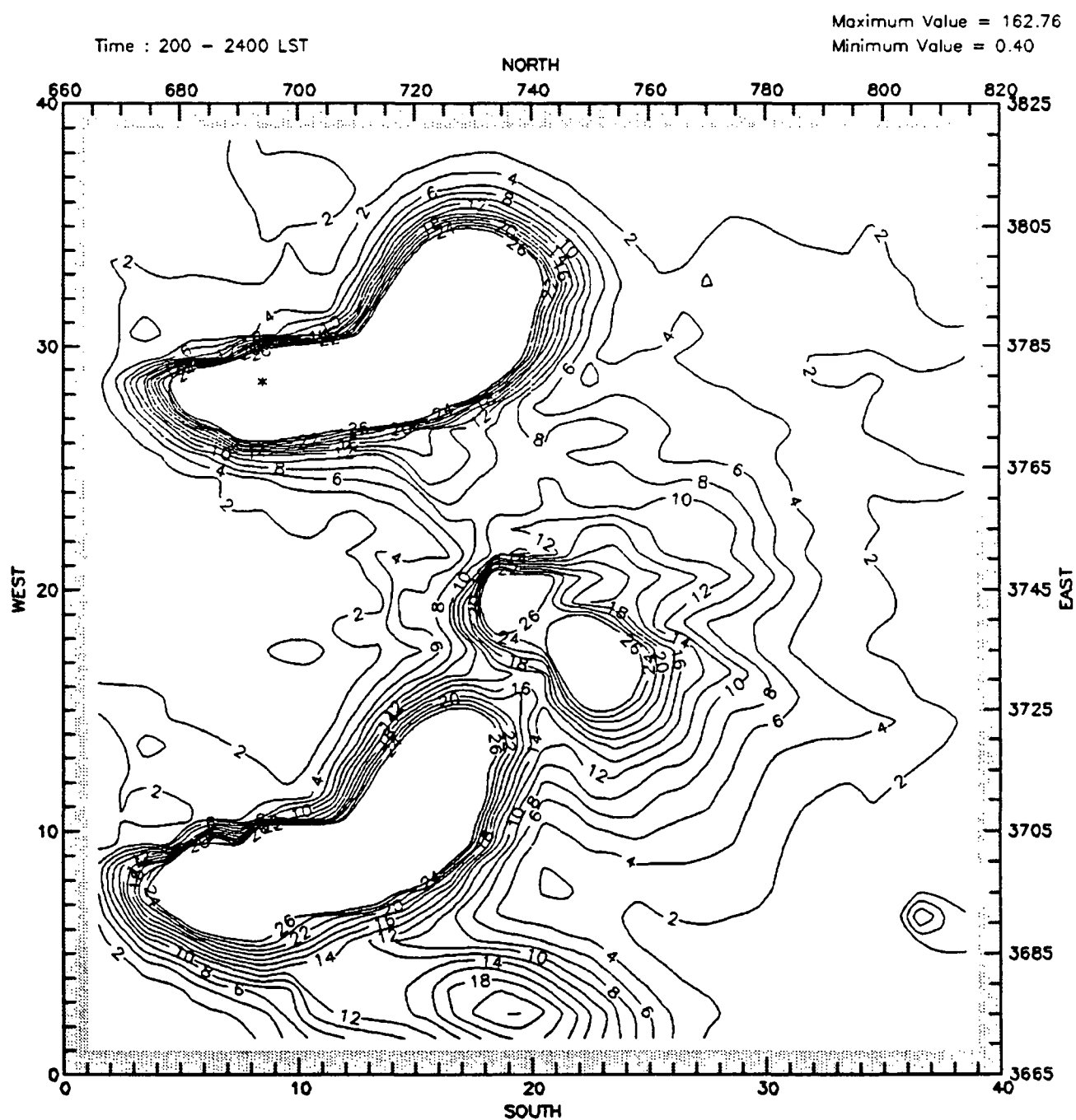
FIGURE 5-12b. Predicted daily maximum NO$_x$ concentrations (ppb) in Atlanta on June 4, 1984 for the 1994 emissions scenario (1) mass emissions calculated by the MOBILE 4 program modified to reflect the effects of HiTEC 3000 and (2) hydrocarbon speciation based on commercial fuel plus HiTEC 3000.